ANILINE
AND ITS DERIVATIVES

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PREFACE

This book is intended for the student of chemical engineering as well as the graduate engineer or works chemist. The technique in the production of Aniline has been used as a vehicle for presenting to the reader the business of plant chemistry. Too often instruction in industrial chemistry is not given the business background that it requires, for more than any other engineering profession, chemistry must emphasize economy of operation.

It is not sufficient for the chemical engineer to study the underlying reactions of a process, to construct a plant based on such findings, and to supervise the operations for the production of a satisfactory product—he must also assume responsibility for the most economical conversion of raw materials to finished product, in order to insure the existence and continuation of the industry.

Most of the works on chemical engineering have emphasized the nature and construction of plant apparatus in conjunction with the elementary processes used in industrial chemical operations. This work endeavors to take up the train of thought at this point to present the application of these principles of chemical engineering as found in well-organized chemical activities. Stress has been placed upon plant investigations in an effort to show how the results of such research are used in determining operating policy.

The importance of plant control through the medium of the laboratory has been elaborated under the title of "The Chemical Budget." Here the entire operation is compared to the budget system adopted by all progressive modern business organizations. As a business cannot be conducted without expense, so also operations cannot be conducted without losses of essential materials. That it is possible to confine these expenditures or losses of materials to legitimate calculated limits is the hope of the successful executive, or chemical engineer.

Upon this hope the prospect of profit is based, and upon its fulfillment as evidenced in the cost sheet are the business man and industrial chemist appraised.

Other phases of operation are duly emphasized. The underlying theory and the by-product poisoning are fully discussed. Physical constants, chemical behavior and commercial uses are noted; so that the reader, student or executive, may use the work as a business reference in the manufacture of aniline, its derivatives, or other chemical products.

In discussing the manufacture of the derivatives of aniline, the author has treated only lightly underlying theory and group reactions, and has endeavored rather to emphasize technique in the handling of materials. For this reason he has included the chapter on the "Action of Acids and Alkalis on Engineering Materials." This chapter should meet a long-felt need for a quick reference in planning for new construction.

The author must acknowledge many sources of assistance in the preparation of the manuscript. He has consulted practically all the recent literature and the works of Fierz-David, J. C. Cain, Lange, and R. N. Shreve; he is however particularly grateful to present and former associates engaged in manufacturing and research problems for making this volume authoritative and reliable by their practical advice and helpful suggestions. Especial thanks are due to Dr. Alfred Müller for assistance in preparing the notes on direct black E. W.., amino azobenzene, and indigo; to Arthur Hough for authoritative information regarding the manufacture of nitrobenzene; to Dr. C. L. Knowles for contributing the chapter on "Physical Constants of Aniline"; to many prominent manufacturers of aniline and its derivatives for their cooperation in reading the proofs and making valuable suggestions; and finally to Dr. John C. Olsen of the Brooklyn Polytechnic Institute for mature and sympathetic advice in the preparation and arrangement of the material contained herein.

P. H. GROGGINS

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CHAPTER I

INTRODUCTION *

The coal tar industry holds a unique position in the industrial world, as it is entirely the outcome of scientific research. The first seed was planted in 1825 when Faraday discovered benzene, which he obtained from the liquid products condensed on compressing the gas obtained from coal oil. A year later, 1826, Unverdorben obtained aniline by the mere distillation of indigo and called it "crystalline." Runge afterwards obtained it from coal tar oil and, having observed that it produced a violet blue coloration with chloride of lime, called it "kyanol." It was subsequently obtained from indigo by Fritsche by distilling this coloring matter with caustic alkali. Mitscherlich later obtained benzene from benzoic acid and from this produced nitrobenzene, this discovery paving the way for Zinin, who showed that benzidam (aniline) could be produced by the action of sulphuretted hydrogen in the presence of ammonia on an alcoholic solution of nitrobenzene.

Hoffman, in his first published paper, showed that Unverdorben's crystalline, Runge's kyanol, Fritsche's aniline and Zinin's benzidam were all the same compound, and for which he selected Fritsche's name Aniline. His work on the separation of aniline from coal tar started in 1843, and continued after his arrival in England in 1845, and it is remarkable to learn that practically all of the aniline used for his numerous researches was obtained by the laborious and the costly process of distilling indigo with potash.

At this time, 1843, organic chemistry was still in its infancy as coar tar naphtha had not yet been investigated. Runge had isolated phenol, aniline and quinoline. Naphthalene was known

* Abstract—Perkin and Armstrong, Hoffman Memorial Lecture. Trans. of Chem. Soc., 1896.

to exist in the tar, having been separated by Garden as early as 1820 and finally Dumas had discovered anthracene. This was about all that was known of the composition of coal tar at that time. In 1845 Hoffman showed that benzene must exist in coal tar naphtha, as he found that aniline could be produced from it. Upon his suggestion Charles Mansfield undertook to investigate the liquid hydrocarbons of coal tar and after much patient and persevering experimentation finally produced benzene and toluene in a pure state. From the latter Hoffman produced toluidine.

Amongst the investigations carried on by Hoffman were the classical "Researches Regarding the Molecular Constitution of Volatile Organic Bases," in which he succeeded in displacing the hydrogen of the NH_2 group by different alcohol radicles, eventually obtaining also the ammonium compounds. Thus (J. Chem. Soc., 3, 1851) he describes ethylaniline, diethylaniline and methylaniline.

Hoffman's memory, however, will be revered not so much for his personal contributions to the early chemical literature as for his marked influence and inspiration as a teacher upon a host of brilliant chemists who studied under him and had the pleasure and benefit of his personal advice and encouragement and who later united in referring to him as the Pioneer and Leader of coal tar chemistry. There can be no doubt that his researches on coloring matters have had a determining effect on the course of the development of the color industry. To Perkin (one of his students), however, belongs the credit for the introduction and development of the industry, for he quickly realized the commercial importance of the numerous discoveries in coal tar chemistry which now followed in a tumultuous succession.

During his Easter vacation, 1856, while experimenting on the futile task of attempting the preparation of quinine from allyltoluidine, he found that no promising results could be obtained by converting the latter to a salt and treating with potassium dichromate. His interest in the reaction persisted,

however, and he decided to repeat the experiments with a simpler base. Aniline was selected, and its sulphate was treated with potassium dichromate; in this instance a black precipitate was obtained, and on examination was found to contain the coloring matter since so well known as aniline purple, or mauve. Very soon after this discovery (made in his rough laboratory at home) Perkin found that it had the properties of a dye and resisted the action of light very well. He then managed to have Messrs. Pullar, of Perth, test out some specimens of dyed silk, and from them received the reply following, which shows the state of the dyeing trade at that time, June, 1856.

> "If your discovery does not make the goods too expensive it is decidedly one of the most valuable that has come out for a long time. This color is one which has been very much wanted in all classes of goods and could not be obtained fast on silks, and only at great expense on cotton yarns. I enclose you a pattern of the best lilac we have on cotton. It is dyed only by one house in the United Kingdom, but even this is not quite fast, and does not stand the tests as yours does, and fades by exposure to air. On silk the color has always been fugitive. It is done with cudbear or orchid and then blued to shade."

Considerable difficulties were met; first, in dyeing cotton, as no suitable mordant had been discovered for this new coloring matter and only the pale shades produced by the natural affinity of the dye for the vegetable fibre were obtained. Then fears were entertained that it would be too costly and finally prejudice against a new material that did not behave as the old products did had to be overcome. Despite the dissuading advice of Hoffman, Perkin, at eighteen, left college to continue his investigations and to proceed with the production of this dyestuff. A general patent was taken to include the oxidation products of salts of aniline, toluidine, zylidine and cumidine.

In June, 1857, with the assistance of his father and friends, construction of a plant at Greenford Green near Harrow to manufacture dyes was commenced. None of the backers of the proposition had ever seen the inside of a chemical works. There was no standardized production equipment to select from, as

the character of the operations to be performed was so entirely different from anything then in vogue. Only impure benzene could be obtained, and this varied greatly in quality. No nitric acid strong enough for the preparation of nitrobenzene could be obtained commercially, and as there was no desire to complicate the infant undertaking by manufacturing this substance, experiment were made using a mixture of sodium nitrate and sulphuric acid, using the latter in larger proportions than necessary to give an acid sodium sulphate. This method was troublesome at first, but was finally conquered, and very large quantities of nitrobenzene were made this way, this being the first time that nitrobenzene was prepared in iron vessels.

It was only three years before the above-mentioned works were started (1854) that Bechamp showed that finely divided iron borings and acetic acid were capable of converting nitrobenzene into aniline. Had it not been for this discovery the coal tar industry could not then have been started.

In a short time, however, aniline purple proved itself to be an important coloring matter which could be produced on a manufacturing scale. It attracted much attention and, as a consequence, many others commenced its manufacture. Investigation followed investigation, patent followed patent, and new manufacturers with new shades and new dyes made their appearance. The little works at Greenford Green soon found that it could no longer keep pace with the constantly increasing demands and before long France and Germany were laying down the foundations upon which to build the gigantic dye industry that now enriches these nations.

The following prophetic article* appeared in the North American Review, for March, 1896. Subsequent events and today's march of progress both bear out the far-sighted vision of its author.

> "It is fair to hold that the country that has the best chemists will in the long run be the most prosperous and the most powerful. It will have at the lowest cost the best

* "Chemists as Leaders," Peter Townsend Austin.

food, the best manufactured materials, the fewest wastes and unutilized forms of matters, the best guns, and strongest explosives, the most resistant armour. Its inhabitants will make the best use of their countries' resources; they will be the most healthy, and the most free from disease; they will oppose the least resistance to favorable evolution; they will be the most thrifty and the least dependent on other nations. The education of its people in chemistry and the physical sciences is the most paying investment that a country can make. Competition today between nations is essentially a competition in the science and applications of chemistry."

CHAPTER II

DISCUSSION OF REACTION

Aniline is prepared commercially by the reduction of nitrobenzene. This reduction is brought about progressively by the action of iron and ferrous chloride. If hydrochloric acid is used there is a temporary, more or less violent evolution of hydrogen gas and steam until the acid has combined with free iron to form ferrous chloride and with any aniline present to form its salt. The aniline hydrochloride in the presence of an excess of finely divided iron becomes quickly hydrolyzed and the free acid liberated combines at once to regenerate ferrous chloride.

Considerable discussion regarding this reaction has taken place, particularly in order to explain the consumption of less acid or chloride than the amount called for by the formula. If we represent the reduction taking place as follows:

$$C_6H_5NO_2 + 6H = C_6H_5NH_2 + 2H_2O$$

then the above formula implies to the presence of hydrogen in molecular quantities and calls for the presence of sufficient hydrochloric acid for its generation. But in practice only about one-sixtieth of the acid required by the equation

$$C_6H_5NO_2 + 2Fe + 6HCl = C_6H_5NH_2 + 2FeCl_3 + 2H_2O$$

is actually used. Operating practice has shown that instead of using 2,136 pounds of acid required by the above formula for a 1,200 lb. charge of nitrobenzene only one-sixtieth or 36 pounds actual HCl (or 120 lbs. of 30 percent solution) are used.

The presence of free acid or alkali and of nascent hydrogen which were long considered essentials in the reduction processes practiced in the plant and in the laboratory is shown now by large scale production to be no longer necessary. Either ferrous or ferric chloride can be used. Such manufacturing evidence is quite sufficient proof that the chloride radicle combines temporarily with the aniline already formed only to be

regenerated upon the addition of more iron when the reaction shows that the intermediate products have been formed in the reducer.

1. O. N. Witt in 1887 suggested the following formulæ as an explanation of the small consumption of hydrochloric acid in the technical process of reducing nitrobenzene compounds by means of metallic iron:

$$24FeCl_2 + 4C_6H_5NO_2 + 4H_2O = 12Fe_2Cl_4O + 4C_6H_5NH_2$$
$$12Fe_2Cl_4O + 9Fe = 3Fe_3O_4 + 24FeCl_2$$

According to this the ferrous chloride formed is the real reducing agent, its action being due to its conversion into a basic chloride, whilst by metallic iron it is constantly being regenerated to ferrous chloride. The above symbolic expression, however, does not account for the generation of hydrogen nor for the reaction between nitrobenzene and iron to form aniline and ferric hydroxide.

2. Wohl * suggested the following formulæ for expressing the reduction equation:

$$\text{I—}\ C_6H_5NO_2 + 2Fe + 6HCl = C_6H_5NH_2 + 2FeCl_3 + 2H_2O$$
$$\text{II—}\ C_6H_5NO_2 + 2Fe + 4H_2O = C_6H_5NH_2 + 2Fe(OH)_3$$

The above equation does not account for the formation of the magnetic iron oxide Fe_3O_4 as an end product. It appears also that equation No. II should probably be the initial reaction as it has been determined (when reducer machines have stuck) that the charge swells up during the feeding stage and that considerable iron hydroxide is formed. It is this formation which accounts for the heavy load during the early feeding stage; the sludge after complete conversion to magnetic iron oxide seldom if ever gives transmission trouble, even after long periods of settling.

3. Raikow † makes the following suggestion as explaining the reaction:

$$\text{I—}2C_6H_5NH_2 + FeCl_2 + 2H_2O = 2C_6H_5NH_2 \cdot HCl + Fe(OH)_2$$
$$\text{II—}2C_6H_5NH_2 \cdot HCl + Fe = 2C_6H_5NH_2 + FeCl_2 + 2H$$

* J. S. C. I., 1894, Vol. 13, 876.

† Zeitschrift, 1916, Vol. 29, pp. 196–199.

Reaction I above appears to be a correct interpretation of the catalytic part of the process and from observation apparently follows the primary reaction as expressed by Whol in his second equation.

If we now use the latter as a starting point:

$$(a)\ C_6H_5NO_2 + 2Fe + 4H_2O = C_6H_5NH_2 + 2Fe(OH)_3$$

which from observation apparently takes place, then the aniline formed will combine readily with any chloride present thus:

$$(b)\ 2C_6H_5NH_2 + FeCl_2 + 2H_2O = 2C_6H_5NH_2 \cdot HCl + Fe(OH)_2$$

It appears from the above that there is an accumulation of $C_6H_5NH_2 \cdot HCl$ and $Fe(OH)_2$ as intermediate reaction products, and the continuation and completion of the reaction then depends on the addition of more iron, first to convert ferric hydroxide of equation (a) to ferrous hydroxide and finally:

$$(c)\ 2C_6H_5NH_2 \cdot HCl + 2Fe(OH)_2 + 2Fe = 2C_6H_5NH_2 + FeCl_2 + Fe_3O_4 + 2H_2$$

This final action yields end products in accordance with actual operating conditions. It is quite evident to the operator feeding the machine that each addition of iron results in a quick reaction yielding hydrogen and steam, the latter due to the extreme exothermic action. The sludge is practically all magnetic iron oxide with small amounts of ferrous chloride. The ferrous chloride is again regenerated by the final reaction and is again ready for further activity. The amount of free iron in the sludge depends entirely on the excess used to hasten the operation. The reaction expressed in Equation (a) takes place only to a slight extent at boiling temperature, otherwise the use of acid would not be necessary to complete the reduction. The extent of the reaction increases, however, with a rise of temperature and pressure. (See process Dr. Conway; page 148.) The action of water on finely ground cast iron even in the presence of iron salts may be observed quite distinctly long after the reduction is complete by the vigorous evolution of hydrogen.

Equation (*b*) shows that any aniline formed by the preliminary reaction combines immediately with the ferrous chloride present to form aniline hydrochloride, with ferrous hydroxide as an intermediate product. Equation (*c*) shows that in the presence of an excess of metal the neutral hydrochloride is quickly hydrolyzed, and the acid thus liberated combines at once with new iron to regenerate ferrous chloride. This free acid liberated by the hydrolysis of neutral salts (according to Raikow) has this power of causing an increased activity of metals towards water. It is evident that a slight excess of iron is consequently always necessary to bring about the regeneration of the ferrous chloride and thus insure against any intermediate reduction products (axoxy, azo, and hydrazo) remaining in solution, incompletely reduced. Practical confirmation of this interpretation is the use of aniline hydrochloride (mother liquors) in the reducers in place of acid to carry on the reduction.

Bearing in mind the practical effects of the formulæ advanced to explain the reduction of nitrobenzene to aniline, it is well to remember that the addition of hydrochloric acid generates a large volume of hydrogen as soon as it reacts, and the exothermic reaction manifests itself in considerable steam pressure. It is, therefore, advisable not to add too much acid at once, the best procedure being to add a smaller quantity at frequent intervals. When ferrous or ferric chloride is used, no such violent reaction is encountered, as the first reaction results in the formation of aniline and ferric hydroxide, by the action of finely divided iron on nitrobenzene in the presence of water. In the latter method it is advisable, in order to simplify procedure, to charge up the reducers with the entire charge of nitrobenzene and half of the chloride. This practice produces an initial reaction which is maintained by the continuous feed of iron. The reaction temperature is then kept up and the reduction thus proceeds more rapidly.

From the above discussion, it would appear that a very small quantity of ferrous chloride could keep on reacting to effect the

necessary reduction. In fact, this is true, but manufacturing practice necessitates the addition of the acid or chloride in such quantities that the reaction will take place in the shortest possible time, compatible with standardized operating conditions and due observation of the laws of safety.

It is evident that the ferrous chloride here acts as a catalytic agent, constantly combining with the aniline as it is formed, to make the reducto-active aniline hydrochloride only to be regenerated again upon the addition of more fine iron.

CHAPTER III

OUTLINE OF MANUFACTURE

A. Reduction Equipment

The reduction operation is carried on in cast iron kettles of all sizes, the larger ones finding greater favor owing to their more economical operating cost. The standard kettles, made by

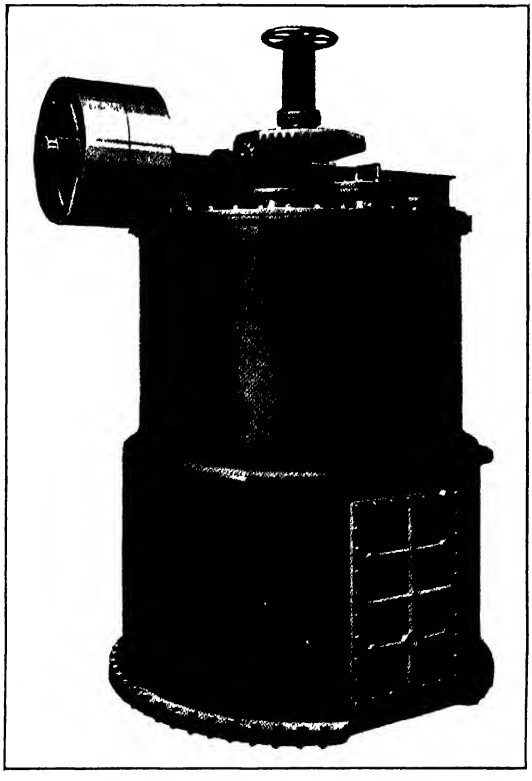


FIG. 1.
Reducer (Jacketed).
1600-gallon capacity. Fitted with device to raise rabbles out of sludge. (Made by Bethlehem Foundry & Machine Co.) Step bearing.

any of the prominent manufacturers, will resemble one another quite closely. Each manufacturer, however, has introduced one or more refinements, calculated to appeal to the experienced

chemical engineer. The dimensions of a 1,600 gallon reduction kettle in which 5,000 lbs. nitrobenzene can be reduced will be closely as follows:

Diameter inside	6 ft. 2 in.
Depth inside	8 ft.
Height over all	10 ft. 4½ in.
Floorspace	8 ft. 7 in. x 6 ft. 6 in.
Pulley	30 in. x 9 in.
Gear ratio	50 x 18
Pulley speed	110 R.P.M.

The machine is equipped with side and bottom cast iron lining plates. These can be reversed or replaced in order to protect the apparatus against the continuous wearing action of the iron borings. A side door in the reducer permits the removal of the liner plates. Some manufacturers of aniline oil are now lining their reducers with acid-proof brick or tile. This lining lasts almost indefinitely, and works very satisfactorily. A specially designed reducer blade carries plows which can be removed or replaced through the side door of the reducer. The machine is equipped with a nozzle at the base so that the residual sludge (after the reaction is completed) can be washed out. As a considerable loss can be incurred if the seal on these nozzles is not tight, care should be exercised in selecting or designing a nozzle calculated to meet practical operating requirements. The nozzle should be so designed that it can be operated from a safe distance, so as to avoid scalding while dumping charges. The clamping arrangement should be such that a tight seal is assured. Experience has shown that a long dumping nozzle is conducive to a restricted passage as sludge quickly accumulates at this point. A practical arrangement is to have the nozzle made of wood, protected front and back with steel discs and practically flush with the outside of the casting. The wood plug is carried by a long screw encased in a cast iron box surrounding the clean-out hole, making it possible to operate at a safe distance, and at the same time insuring a positive seal.

The steel shaft is driven by cut steel gears, placed on top of the reducers. These bevel gears may be placed so that the drive gear is underneath or above, the machine as a rule running more quietly when the former arrangement is used. The shaft can be supported in two ways and rival manufacturers advance reasons supporting the superiority of their design. The shaft in some reducers is supported by a special step bearing at the base of the machine, and by the collar and thrust bear-

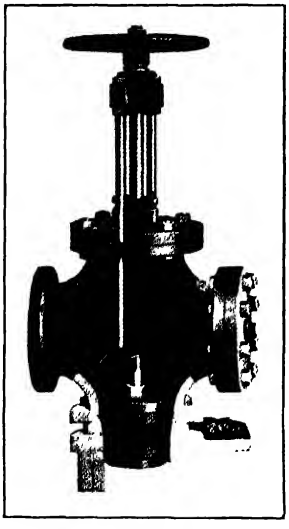


FIG. 2.
Reducer Discharge Valve.
Fully enclosed, quick acting, wooden contact for seal.

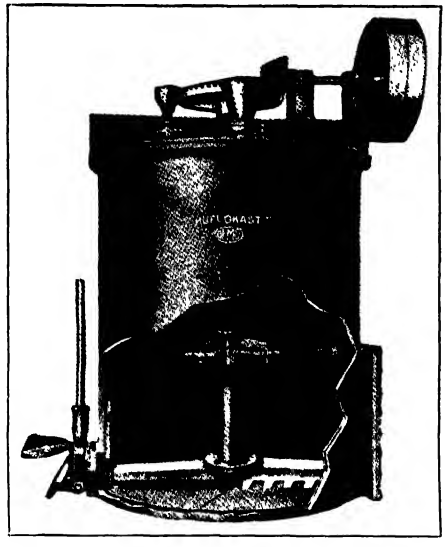


FIG. 3.
Reducer (Jacketed).
1600-gallon capacity, with bearing in the yoke, hollow shaft and agitator for admitting steam.

ing on top. In others it is supported by a heavy bearing in the yoke midway in the reducer. The designers of the former contend that the heavy duty encountered and the possibility of large pieces of worn iron pipe or cakes of sludge falling into the machine require a step bearing. They also point out the difficulty in making a suitable yoke bearing that will withstand the constant erosive action of the iron borings, without soon causing a decided wobbly action on the part of the agitator.

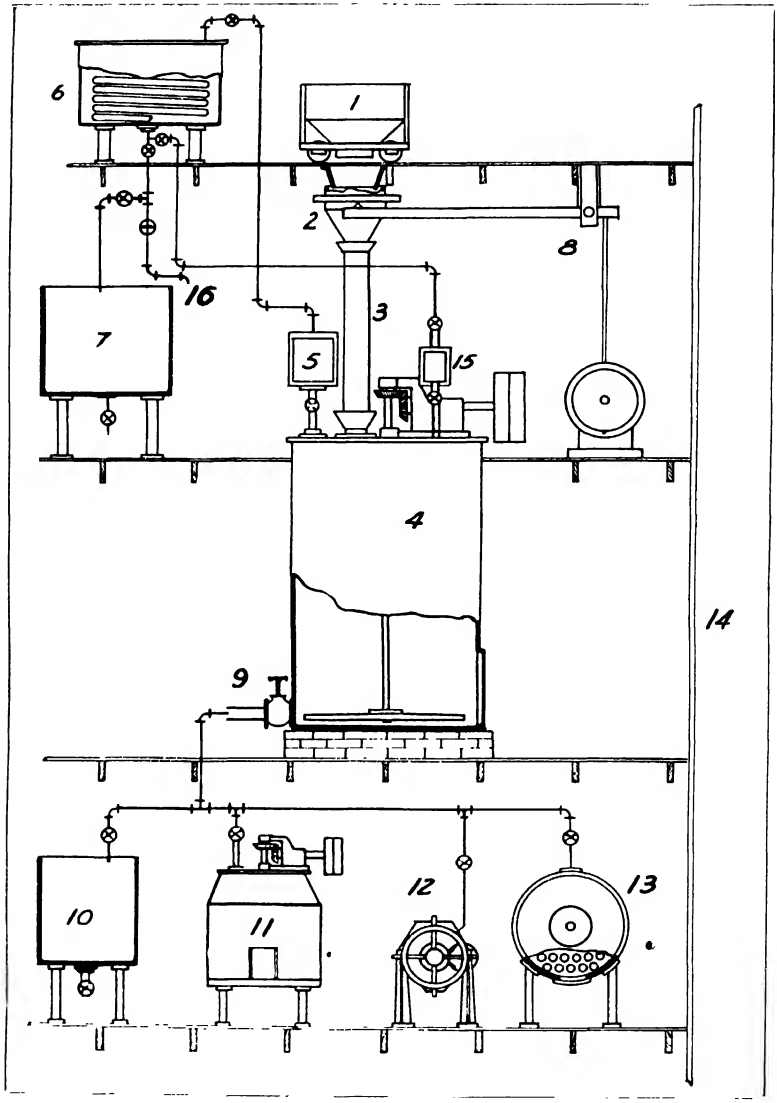


FIG. 5.

Reducer House. Arrangement of equipment:

1, delivery car for iron borings; 2, hopper and automatic feeder; 3, iron borings delivery line; 4, reducer; 5, baffle box; 6, condenser. Note connections at base for refluxing or for distilling into. 7, crude receivers; 8, weighing apparatus for iron borings; 9, outlet valve to reducer leader to either; 10, ordinary receiver used in syphon system; 11, vacuum distilling kettle; 12, filter press, or 13, horizontal vacuum still; 14, elevator shaft; 15, sight box on reflux line; 16, safety drip which is kept open during reflux period to prevent contamination of system with nitrobenzene.

line receivers. An additional safeguard on this line is the drip valve beyond the main valve. This drip is kept open whenever the main valve is closed, so that any leakage at this point can be quickly detected and at the same time prevent any contamination from nitrobenzene taking place. Operating experience has proved conclusively that even the smallest quantities of nitrobenzene in the aniline will discolor it and give it a yellow cast. Laboratory results show that the nitrobenzene impurity content must be less than 2/100 of one percent in order to keep producing a water white aniline.

During the reflux, the distillate is run into the sight box on the reducer and the operator here observes the progress of the operation. When the charge is reduced the valve to the reducer is closed and the distillate diverted to the distilling tank. This tank is set up sufficiently high on the operating floor to permit any sludge in it being returned to the reducer to be reworked. This arrangement also permits of the easy disposal of any contaminated charges in the event of "stuck machines." It also gives the operator an opportunity to follow the rate of distillation and thus helps to avoid overrunning of tanks.

B. Feeding the Reducer Charge

In order to enable the reader to appreciate more fully the fundamentals and the development of the aniline industry and particularly to enable him to have a basis for studying the chapter on "Survey of Processes" the following "Outline of Manufacture" is presented so as to follow quite closely the orthodox method as described only scantily in some texts. This method calls for the use of non-jacketed (usually small) reducers from which the aniline is distilled by the use of live steam after reduction is completed. This scheme is, of course, quite archaic (although still used by several manufacturers) as it gives rise to the production of a very large quantity of aniline water. The treatment of this aniline water entails a very large expense and causes a considerable loss in yield. The aniline oil after it is distilled out of the reducer is sent to the distillation house for

separation and rectification. The residual sludge in the reducer is dumped and disposed of in the most convenient manner.

The reducer is inspected to insure proper mechanical operation and the dumping nozzle is then sealed. The reflux valve from the condenser and the vent valve over the sight box are opened and at the same time the valve to the distilling tank is closed and the adjoining safety drip opened. The machine is warmed up so that the reaction will proceed more rapidly. The charge of nitrobenzene is then blown into it from the scale tank, usually located on the ground floor. The valves operating this tank are near the reducer so that the procedure can be properly supervised without leaving the machine.

The advantage in keeping the nitrobenzene tank below the reducer is the prevention of contamination due to leaky valves when the oil is run in by gravity. After the oil is in the reducer, the charge of iron chloride, aniline salt, or acid is partially added; followed by an initial feed of 200 pounds of iron borings and about 100 pounds of aniline water. The machine is now run on this initial feed until the charge starts " coming over " and is visible in the sight box. The iron is then fed in regularly so that boiling temperature is maintained and the distillate comes over at a fair rate. If the temperature is too low, azoxy compounds are formed, which are reduced only with great difficulty. When the reflux proceeds too rapidly feeding is stopped until the pressure subsides. A full flow of water is maintained on the condensers while the entire charge of iron is introduced. About three hours is required to feed a charge of 1,200 pounds and about 10 hours for a charge of 5,000 pounds of nitrobenzene.

The feeding process is not difficult from an operating point of view. Smoothness of reaction is invariably obtained if the iron be of a uniform quality and feeding done at definite intervals. It is much better to feed small batches at frequent intervals than large quantities at more distant periods. The feeding of smaller batches practically precludes the possibility of machines sticking, and also yields a more finely divided sludge. This method seldom gives rise to undue reducer pressures.

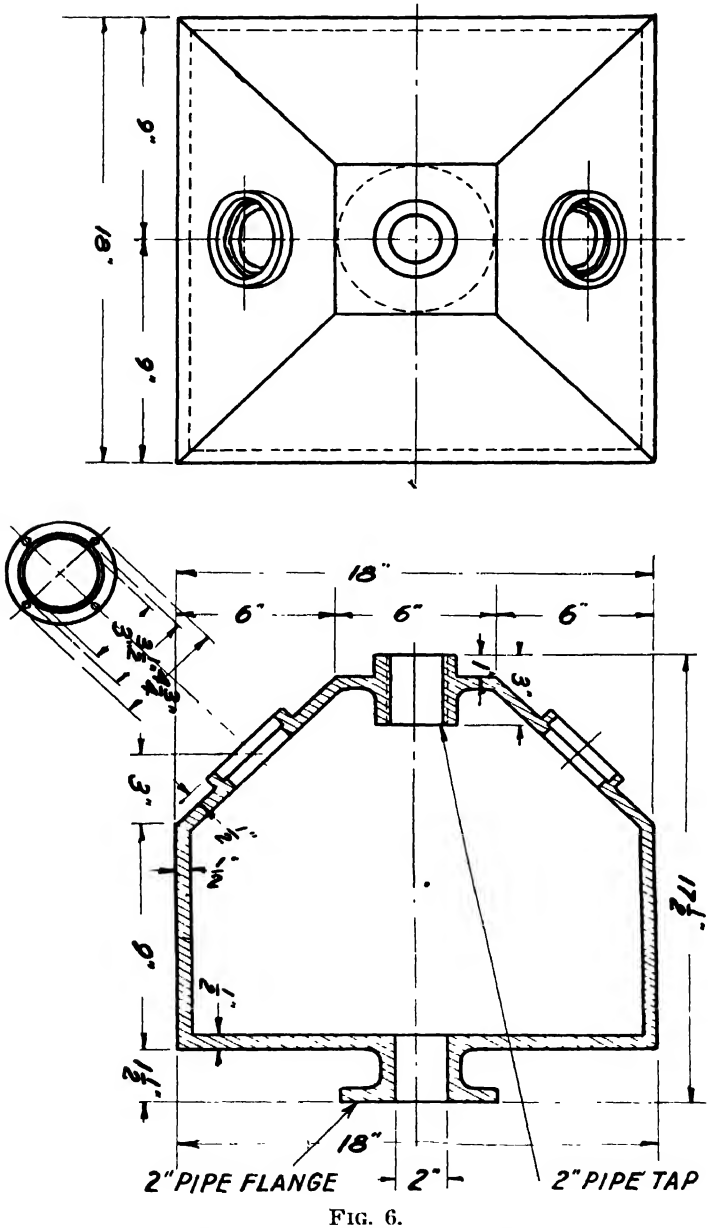


FIG. 6.
Reducer Sight Box, showing observation holes.
An electric light is placed at one of the ports.

The operator must watch the sight glass before removing the funnel plug to feed iron. When no pressure appears in the glass, the plug is manipulated in the funnel which contains the batch of iron borings until the iron starts to drop. Water is turned into the funnel to help wash down the iron and to clean out the hole so that the plug can be properly seated. As soon as the borings are washed into the reducer the funnel is again filled for the next feed. This practice cuts down to a minimum the amount of fumes escaping from the reducer. However, the feeding operation in some plants is greatly simplified by the introduction of a very efficient type of condenser, which has the effect of creating a slight vacuum on the reducer. This condition then permits of a continuous feed of iron through a funnel in which a wooden plug is loosely suspended. The condenser coil referred to is designed so that the aniline vapors pass on the outside of a network of closely laid lead coils, through which water circulates at a high velocity. This arrangement eliminates oil, slime and rust accumulating on tubes in condensers of the ordinary type.

When ferrous chloride is used some operators make it a practice to add the chloride to the batch of iron borings and feed both ingredients together.

The presence of free benzene in the nitrobenzene introduces a difficult problem during the reduction as it necessitates a longer reduction period and the consumption of an abnormally large quantity of iron. Its presence is detected when samples of aniline from the reflux line show the oil floating on top of the water. The oil also smells strongly of benzene. It requires higher temperatures to drive off this benzene into the vent tank and at times the water is turned off the condensers to effect this rise in temperature, and to prevent solution of the benzene in the aniline in the cooling coils. Of course, it is possible to distill off the free benzene into the receiving tanks or into a separate tank, but such a procedure usually means contamination of the system.

It is evident that free benzene is a total loss financially; owing

to the increased consumption of iron and time to effect a reduction, its presence should be guarded against, during the nitration of benzene.*

The presence of dinitrobenzene gives rise usually to a sluggish reduction necessitating at times slightly more acid or chloride to complete the reaction.

There is quite a diversity of opinion as to the best method of feeding in all the ingredients. The method previously outlined was to blow the entire charge of nitrobenzene into the reducer at the start and to add about one-third of the required amount of ferrous chloride crystals, the feeding in this case being the simple addition of iron borings. Some operators advise the addition of iron and nitrobenzene together all along the entire feeding operation. They contend that this practice makes for a more rapid reaction as practically no pressures are realized after the " feed " is well under way. The ferrous chloride in this case is also added periodically. A number of investigators have advised putting all the nitrobenzene and all the chloride in at the start. Such a practice although simplifying the operation often leads to excessive pressures.

A glance at the formulæ underlying the reaction shows quite conclusively that ferrous hydroxide is formed as an intermediate product during the reduction. If the iron is added too rapidly this product accumulates so quickly as to cause " sticking " of machines. An examination of such a " stuck " machine shows that the mass of iron has largely increased in volume and has become spongy, with a marked absence of the fine Fe_3O_4 sludge which should accompany a properly reduced charge. On the whole, little time is gained by pushing the " feeding " operation, and oftentimes such tactics cause considerable trouble with pressures and consequent aniline losses. It may be said within strict limits of operating data that slight additions to the feeding time cause a corresponding curtailment in the reduction period provided the machine is kept warm at all times.

* A fuller discussion of this subject is taken up in the chapter on "Raw Materials—Nitrobenzene."

Water is of course needed to carry on the reaction, for according to the suggested formulæ, four molecules are required in stage (I) for the hydration of the iron and, later, two molecules are needed in stage (II) for the reaction between every molecule of aniline hydrochloride with ferrous chloride. In practice it is found necessary to increase the theoretical amount in order to make the charge more fluid, to avoid sticking of machines and to facilitate the feeding of iron when using the funnel feed. It is readily appreciated that all water added above the required amount unnecessarily dilutes the charge and consequently requires more steam to distill off the oil after the charge is reduced.

Aniline water from previous charges is usually fed into the machines. The use of fresh water entails greater aniline losses owing to the necessity of working up greater quantities of this aniline water in the water stills. About two percent of aniline is kept in circulation for this purpose and if a loss of one percent is sustained in reworking, a net insignificant loss of 0.02 percent would be the result of using the aniline water. A larger amount, however, would be lost in the aniline water stills when fresh water is used, due to the larger quantity delivered.

Some plants feed the iron into the reducer " under surface " by means of a submerged pipe. The aniline water from the previous charge is run into the funnel to wash down the iron into the reducer. This practice of making an undersurface feed is claimed to entirely eliminate the big bulge of free iron caked around the upper part of the reducer and also to assist in making a more even reaction.

It must be borne in mind, that the reaction during the feeding stage is extremely exothermic (about 1,900 B.T.U. being liberated per pound of nitrobenzene reduced) and it is therefore necessary to provide the most efficient type of condenser to take care of the largest volume of reducer vapors possible. This permits not only of a very rapid reduction but also of a saving of considerable steam later on, in completing the reduction.

C. Reduction and Steam Distillation of the Charge

After the iron is all fed in, steam is turned on and the charge refluxed at a lively rate. A considerable quantity of the condenser water can be turned off and just enough circulated to condense the gases. If too much water is used, the sample obtained through the sampling spigot on the reflux line will have a greasy appearance.

The water leaving the condenser should be fairly warm and the mixture of aniline and nitrobenzene passing through the sight box should be warm. As the reaction nears completion, the color of the mixture will change from red to orange and later to yellow and finally to white. The charge is then neutralized with lime and boiled vigorously to break up the soluble iron compounds of hydroxylamine which may be present and the valves then set for distilling out the aniline.

Care must be taken that the reaction is not too violent, as it may result in the breaking up of the aniline into benzene and ammonia. Sometimes reduction is retarded, due to free benzene being present in the nitrobenzene. When such a condition arises, the charge should be thoroughly agitated by means of live steam entering the machine and endeavoring to remove the benzene through the 2 in. fume vent leading to the aniline water tanks above.

Another convenient method is to distill down the charge for a few minutes into a special small tank for that purpose. Once the benzene is removed, the reduction will proceed rapidly and, whereas hitherto the aniline in the samples floated on the water, the oil will now quickly settle to the bottom. When the samples are white and no odor of nitrobenzene is present, the reflux and vent valves are closed and the charge is then either distilled down or the aniline oil separated by other means.

Where a separate still is used to remove the aniline the entire reducer charge is dumped into this still, which is provided with suitable agitators and vacuum pump, and the charge then distilled to dryness and the Fe_3O_4 mechanically thrown out into a car.

D. The Distillation

When live steam is used to distill out the oil from the reducer at atmospheric pressures the procedure is as follows:

The reflux line is closed and the line to the distilling tank opened, care being taken to close the safety drip. The steam pressure is then increased to 15–20 lbs. and the live steam line opened so as to maintain a constant volume in the reducer. A full flow of water is now maintained on the condenser which governs the rate of distillation as care should be taken to avoid uncondensed gases from going to the distilling tanks.

This particular kind of distillation (using live steam) is often employed for the separation of a substance whose distilling point is far above 100° C. This phenomenon is explained as follows: If a mixture of two liquids absolutely insoluble in one another is taken, each liquid will exert its own vapor pressure, as it would if it were alone, and will not in any way be influenced by the other. A practical example of this is a mixture of water, B.P. 100°, and aniline, B.P. 184.6°. When this mixture is gradually heated, the vapor pressure of both substances will increase and boiling will begin. When the sum of the vapor pressures of both substances is equal to the barometric pressure, which is assumed to be 760 mm., the mixtures will boil at 98.4°, as will be seen from the following table:

Temp	Vap Press $C_6H_5NH_2$	Vap Press H_2O	Total
98.0	42.11	707.13	749.24
*98.4	42.88	717.58	760.46
98.9	43.84	730.61	774.45

At this temperature a mixture of water and aniline distills over. The proportion of the two substances will be seen from the following considerations.

According to Avogadro's Law, under the same conditions of temperature and pressure, equal volumes of ideal gases contain the same number of molecules. If the temperature is the same and pressure different the number of molecules will be proportional to the pressure. Now considering the mixture as consisting of vapors of water and aniline at 98.4°, at this

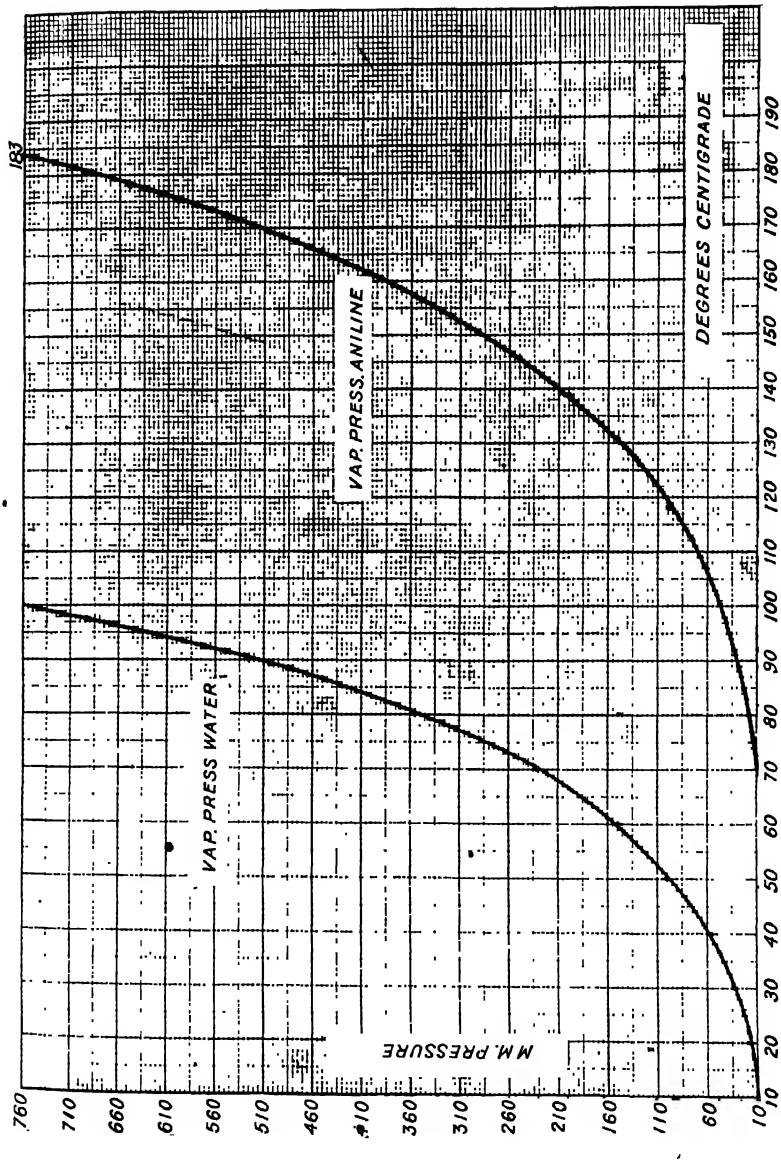


FIG. 7. Vapor Pressure Curves. Water and aniline.

temperature the former exerts a vapor pressure of 717.58 mm. and the latter a vapor pressure of 42.88 mm. The molecular quantities being in the same ratio, for every 717.58 molecules of water, 42.88 molecules of aniline will be present. In order to calculate the weights of the substances that distill over, it is necessary to multiply the number of molecules by the molecular weight of each substance. In the case of aniline, for every 717.58×18 parts by weight of water, 42.88×93 parts by weight of aniline will distill over, which corresponds approximately to 3.2 parts of water to one part of aniline. This proportion should remain constant until the aniline has completely distilled over. As a matter of fact, in the steam distillation of a reducer charge containing about 860 pounds of aniline, 4,960 lbs. of steam are required instead of the theoretical 3,000 lbs. There are several reasons why ideal distillations are not realized. The substances are not absolutely insoluble in one another. Experimental data also show that up to the point of solution the ratio of water to aniline approaches the theoretical (see distillation tables) and when the solution point at 98.4° C. is reached, about 7.0 percent aniline remains in solution. The excess above the theoretical amount of water carried over is due largely to this degree of solubility of aniline and water because about 10.5 parts of water to one part of aniline are distilled over after the solution point is reached.

Also since the heating is carried out by steam and the temperature of the substance is never raised to the exact boiling point, the mean temperature is somewhat different from that given above, and the proportions are therefore altered.

The steam distillation is carried on until samples from the condenser show that practically all the aniline has been distilled over and that only a trace remains dissolved in the sludge. In good operating practice only one-tenth of one percent remains in the sludge to be dumped. About six hours time is required to steam distill about 860 lbs. of oil from an 800 gallon reducer.

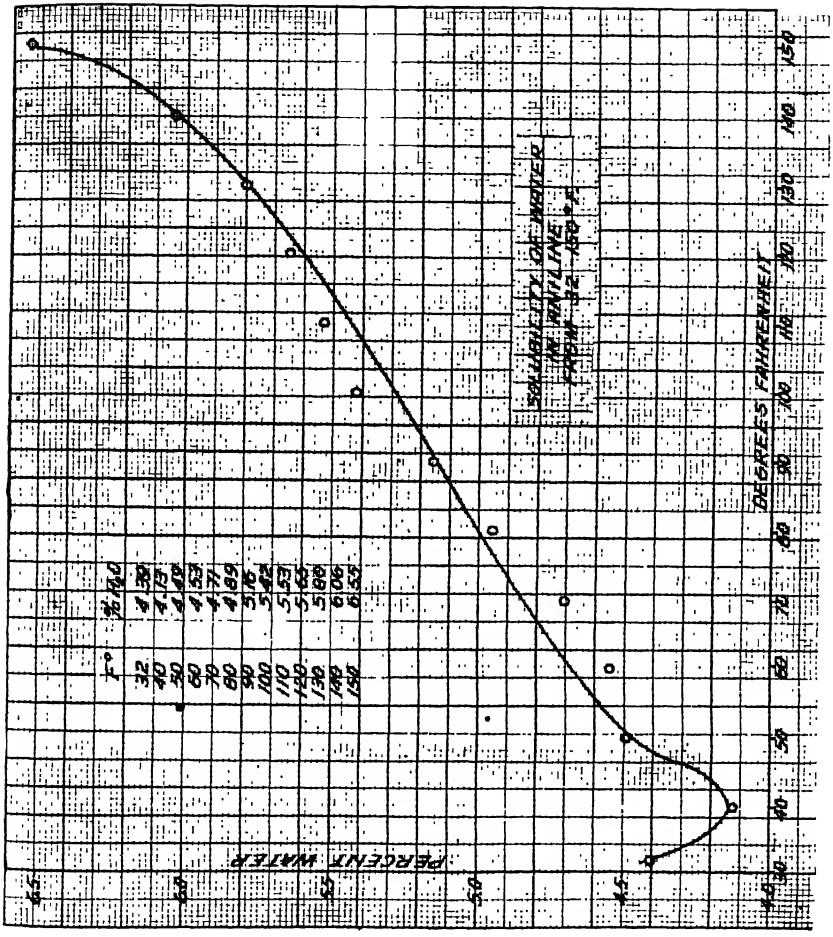


FIG. 8. Solubility Table. Water in aniline.

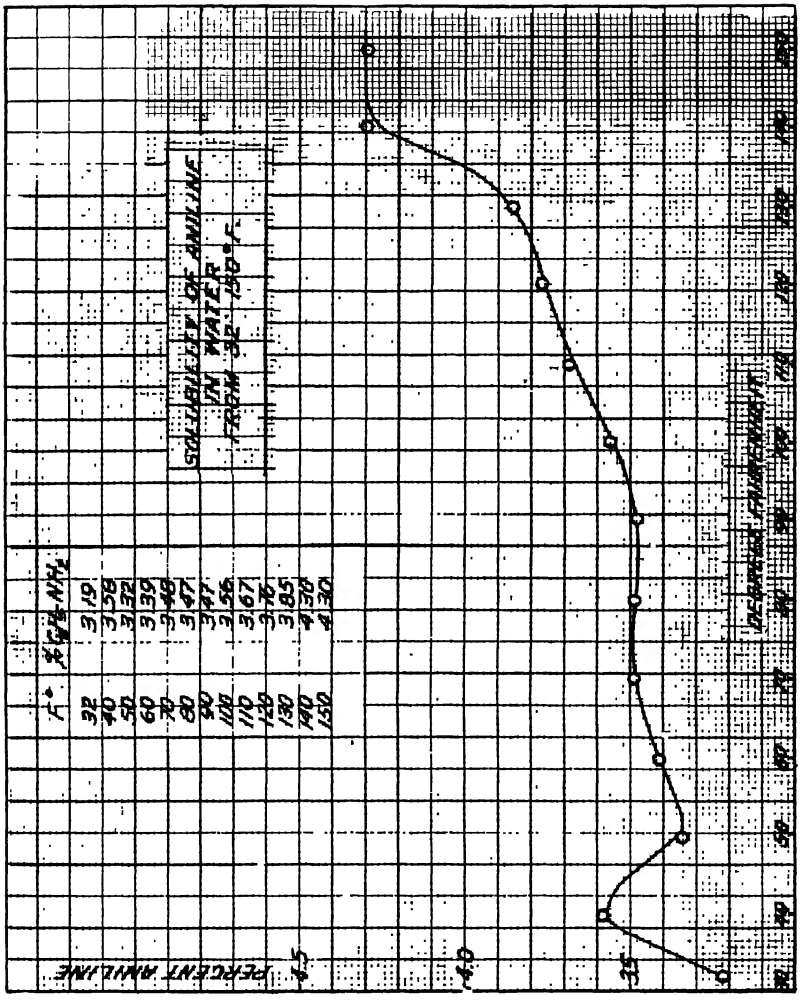


FIG. 8A. Solubility Table. Aniline in water.

PURIFICATION OF ANILINE

Treatment in the Aniline Distillation House

The charges of aniline from the reducer house are pumped to settling tanks in the aniline distillation house. These tanks are ordinary, vertical, steel tanks, usually identical in size with those for collecting the distillate in the reducing house. They are provided with gauge glasses, cooling coils, receiving and delivery pipes, and vents. The charge is permitted to settle for several hours, when the aniline is drawn off from a connection at the bottom to an aniline blowcase. When aniline water makes its appearance the feed to the aniline blowcase is stopped, and the water is then drawn off from an upper valve about 18 ins. from the bottom of the tank and delivered to feed tanks for the water stills. The aniline water between the lower and upper valves contains considerable aniline in suspension and is retained in the tank and the next charge is pumped in on top of it.

The importance of cooling the charges of aniline cannot be overestimated. A glance at the solubility tables shows that above 98° F. the solubility of aniline in water increases markedly and jumps from 3½ percent at 90° F. to 4½ percent at 140° F. This increased solubility is coupled with the fact that the solutions of aniline in water and water in aniline are about the same gravity at 150° F. and consequently unless the solutions are cooled, a large percentage of aniline would be delivered to the water still through incomplete separation.

The aniline water which has been delivered to the feed tanks is dropped by gravity into the water stills. The temperature is raised to 225° F. with about 7-8 lbs. steam pressure and the distillation proceeds until a sample of the residue shows only a trace of residual aniline. The solution must be clear and have no aniline odor, and should not exhibit an oily trace when dropped on a cool surface. In a charge containing 7,000 lbs. of aniline water at 3½ percent oil, about 40 percent or 2,800 lbs. will be distilled over; the balance, 4,200, being dumped. The distillate will be composed of 2,555 lbs. of water and 245 lbs. of aniline; the ratio

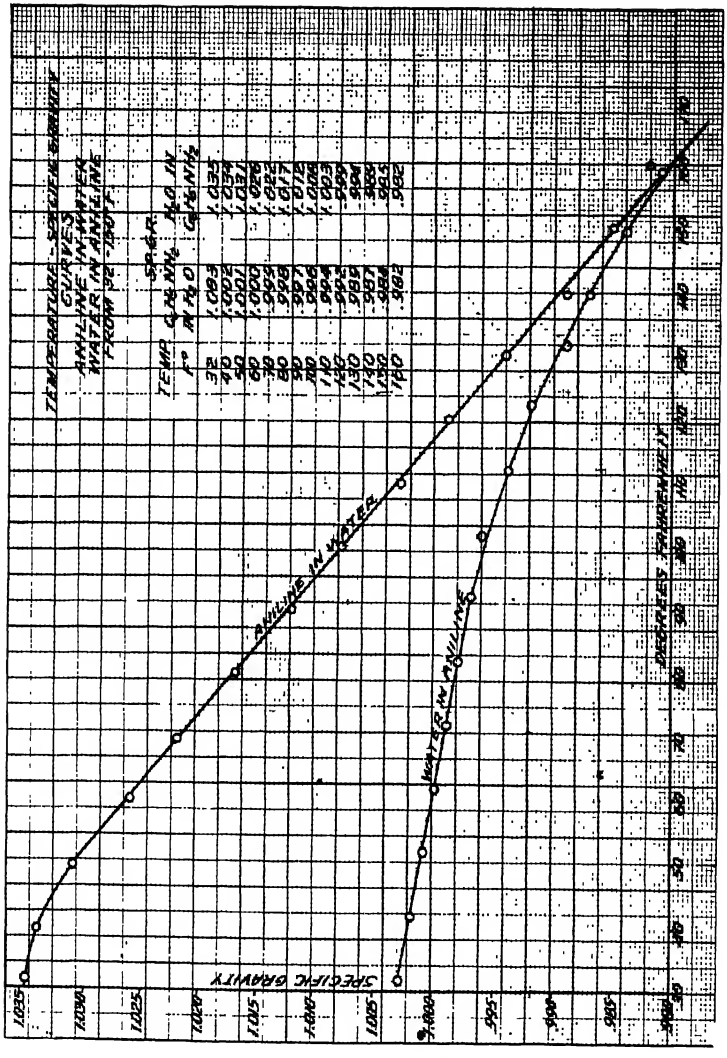


FIG. 9. Temperature-Specific Gravity Curves. Aniline in water; water in aniline.

of water to aniline being distilled over is therefore approximately 10½ to 1.

If an examination of some of the theoretical phases of this distillation are made it would be a simple matter to predict the results of actual operating conditions relative to the amount of aniline water that has to be handled.

Assuming a plant to operate at the rate of 30 reducer charges per day, each charge to deliver 5,000 lbs. of aniline water to the system, a total of 150,000 lbs. of water would be thus accumulated. Now, if a ratio of 10.5:1 aniline to water exists during the distillation of the water, then the following figures would represent the prevailing conditions in treating aniline waters containing respectively 3½ percent oil and 4½ percent oil:

150,000 lbs. × 3½ percent aniline contains 5,250 lbs.
150,000 lbs. × 4½ percent aniline contains 6,750 lbs.

If 10½ parts of water are required to carry off the oil:

55,125 lbs. H_2O will come over with 3½ percent solution
70,875 lbs. H_2O will come over with the 4½ percent solution

15,750 lbs. additional steam will be used for distillation and that amount of additional water kept in the system due to the increased concentration. This figure is equivalent to 10 percent of the total daily water treated in the stills.

The Rectification

The crude aniline delivered from the reducer house and drawn off from the bottom of the receiving tanks into a blowcase is now blown to settling tanks over the rectifier. The oil is permitted to stand for some time until any enmeshed water rises to the top. This is decanted off and the aniline is then drawn into the rectifier by means of a vacuum line. As the bottoms of the settling tanks quickly accumulate a quantity of fine sludge which has to be cleaned out at least once each week, the oil is not dropped in by gravity in order to avoid contamination from sediment that would follow. Sometimes stannous chloride is added to the charge to insure a water white distillate.

About 29 ins. of vacuum is then put on the rectifier and steam is admitted into the coils running lengthwise through it. When the temperature reaches 105° F., water commences to come over and the temperature remains about this point until most of the water is off, this portion of the distillate going to the " crude " receiver. The temperature then rises rather rapidly up to 200° F. when the distillate coming over is largely aniline contaminated by water. This water diminishes in volume until the water bubbles in the sight glass are infrequent. The moisture is then indicated by a flow of the streaky aniline oil. When the flow is clear and white without streaks or bubbles the valves are set so that the distillate runs into the " refined aniline " receivers. The poor grade materials from the " crude " receiver are again returned to the rectifier.

About 30,000 lbs. can be put into each rectifier charge and the amount of pure aniline obtained should be about 85 percent of the charge. Twelve percent constitutes the light aniline and water fraction, the remaining 3 percent consists of a heavy aniline residue which is returned to the reducers and reworked.

The settling tanks and the rectifier should be kept clean at all times in order to obtain the purest grade of aniline. As a rule the rectifier sludge is blown back to the reducers and again worked up.

The Rectifier

This is usually a large, horizontal tank, 8 feet in diameter, supplied with a cleanout head and steam coils. It is lagged with asbestos to reduce to a minimum the amount of heat necessary to carry on the distillation. An 8 inch connection on top of the tank carries the gases to a 12-plate dephlegmator on top of which is placed a water tube condenser. With this apparatus the speed of distillation can be controlled. A second condenser liquefies the gases after they leave the dephlegmator. A sight box placed at the outlet of this condenser affords a convenient means of watching the condition and rate of distillation. By means of the dephlegmator condenser, it is possible to regulate

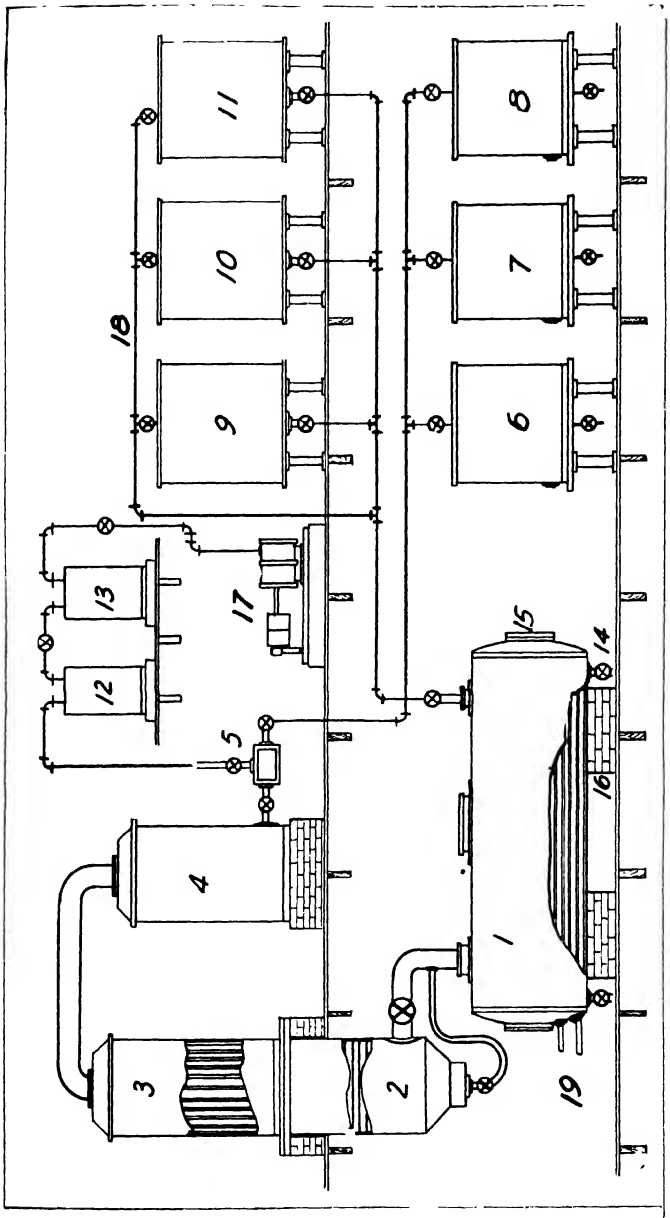


FIG. 10. Aniline Distillation House. Arrangement of equipment:

1, horizontal still, completely lagged; 2, dephlegmator; 3, dephlegmator condenser; 4, condenser; 5, sight box with connection leading to 6, 7, 8, receivers for pure aniline; 9, 10, 11, crude aniline reservoirs; 12, 13, catch-all tanks for aniline vapors; 14, bottom outlet to still; 15, clean-out hole; 16, horizontal steam coils in still; 17, vacuum pump; 18, vacuum feed line from crude aniline reservoirs to still; 19, outside steam connection to still.

the amount of reflux from the dephlegmator back to the rectifier; the return being effected by means of a trap at the base of the dephlegmator, leading to the top of the rectifier. During the final light aniline stage, the flow is slackened so that a better separation can be made. This procedure also makes for a smaller quantity of the " light " oil being distilled. If during the early part of the distillation the temperature is kept high and the rate of flow large, the charge in the rectifier becomes churned so that the entire distillate is more or less contaminated with traces of water.

At all times the cooling condenser must be regulated so that the exit end must feel cool to the hand.

CHAPTER IV

SURVEY OF PROCESSES FOR MANUFACTURE OF ANILINE

The literature covering the manufacture of aniline oil shows that a large number of processes have been developed for separating the aniline from the reducer charge. This separation has in reality been from a manufacturing standpoint one of the greatest problems arising in the preparation of this intermediate. The ideal method if it were possible would be to mechanically separate the aniline oil from the sludge and water —then to separate the water from the sludge so that it would be possible to dump the latter in a dry condition into a receptacle for that purpose. Such a procedure would of course mean the realization of maximum yields, lowest costs, and minimum of handling.

Owing to the mutual solubility of aniline and water and the difficulty in removing aniline from the sludge by mechanical agencies, the problem has given rise to considerable investigation.

The following criteria should guide the manufacturer in the choice of productive equipment for the manufacture of aniline oil:

I. Simplicity—Minimum handling of material.

II. Yields—Reduction to a minimum the apparent sources of loss.

III. Productivity—Schemes for dumping charge directly after reduction and thus practically doubling productivity of reducer.

IV. Water Balance—Elimination of methods that cause accumulation of aniline water, as handling or treating of this involves great losses in yield as well as large power costs.

V. Power Load—Careful consideration to be given to power (steam, air, water, electricity) consumption as considerable variations occur by the use of different systems.

VI. By-product Sludge—In some sections a market can be obtained for a clean dry sludge free from aniline.

In order to derive any results from an investigation as to the most efficient manner of separating aniline from the rest of the charge it would be necessary to make definite assumptions.

1. That the sizes of the reducers are identical in all systems.
2. That the cost of labor for feeding and reducing charges is the same.
3. That the cost of materials entering the reducer is the same.
4. That the efficiency of reduction is uniform.
5. That the reduction of nitrobenzene to aniline is accomplished in all cases by the use of iron borings and ferrous chloride.

The above assumptions are permissible as very little variation occurs in feeding or reducing charges in machines of equal capacity. No comparison could of course be made when large sized machines are used in one case and smaller ones in another, as it is evident that operating labor costs would be less for the former. Also in view of the fact that all things being safe and equal, the time for feeding and reducing charges is proportional to the condensing capacity, it is assumed that all are favored equally.

In order to simplify calculations, the figures used here will be reduced to a unit represented by 1,000 lbs. of aniline made. Aniline losses will be calculated on a basis of 15 cents per pound.

Steam will be charged at the rate of 50 cents per 1,000 lbs. delivered.

DISCUSSION—Method I. Steam Distillation of Aniline from Charge and Treatment of Aniline Water in Stills

Procedure.—After the charge is reduced the valves are set so that the reflux from the condensers above the reducer now feed into the aniline receiver instead of refluxing back to the reducer. From this receiving tank the charge is pumped to settling tanks in the distillation house. Here the charge is per-

mitted to cool and settle, and the oil later drawn off from the lower valves of the settling tanks into the crude aniline blowcase. The aniline water containing from 3½ to 5 percent aniline is drawn off from an upper valve and pumped to storage tanks prior to its being delivered to the aniline water stills. The stills are ordinary horizontal steel tanks in which a number of horizontal steam coils are placed. When the charge in the still has been reduced to about one-half its original content, the distillate shows practically no traces of oil and the balance about 50 percent by volume is ditched. This contains about 0.3 percent of aniline. This percentage can be lowered by distilling longer, but the cost of steam and the probable need for the apparatus for production makes additional distillation beyond 0.3 percent unwise. The distillate is permitted to cool and settle and the free aniline (due to increased concentration) is removed. The aniline water is then again returned to the upper storage tanks and subsequently to the stills. In the stills the reaction is the same; about half of the distillate is recovered, the other half run off. It is evident, and has been verified by plant observations, that an amount of liquid equal to the original volume of aniline water must therefore be distilled. In addition to this considerable steam must be used to supply the heat necessary to raise the temperature of the still charge each time to the boiling point. After careful investigation it was found that two (2) parts of steam would be required for the treatment of every part of aniline water delivered from the reducer house in order to effect the recovery of the dissolved aniline. The cost of separating the oil from the charge by the above method would therefore be—per 1,000 lbs. of aniline:

Cost to steam distill out aniline from the reducer—5,990 lbs. steam at $.50 per 1,000 lbs.	$3.00
Sludge per 1,000 lbs. of aniline = 3,700 lbs. Loss in sludge = 0.2 percent or 7.4 lbs. @ 15 cents	1.11
Loss in aniline water dumped from stills = 5,990 lbs. @ 0.3 percent = 18 lbs.	2.70
Steam required to recover aniline from aniline water = 12,000 lbs. @ 50 cents per 1,000 lbs. steam	6.00
Total cost per 1,000 lbs. aniline	$12.81

It is evident from an outline of this operation that the material has to be handled considerably. The charge also holds up the reducer during the distillation period. In fact this scheme of operation possesses no attractive features; yet it is a fact that it still finds considerable favor among American manufacturers.

Method II. Steam Distillation from Jacketed Reducers

When the reduction takes place in a steam jacketed reducer, a slight improvement is apparent. This is due to the fact that the jacket cuts down the dilution during the reduction period by eliminating the use of live steam in the reducer and furthermore about 1,150 lbs. of water can be returned for use in feeding the next charge. It is assumed that the charge is steam distilled as before owing to the fact that ordinary reduction kettles are not designed to carry the enormous loads arising when the liquid is boiled off through jacket heat. There is a slight diminution in the amount of water produced during the distillation period owing to the increased concentration of the oil in the charge at the close of the reduction period.

The cost of separation is therefore:

Cost to steam distill out aniline from reducer 5,650 lbs steam @ 50 cents 1,000 lbs.	$2 83
Sludge water 3,000 lbs. @ 0.2 percent loss = 6 lbs. @ 15 cents	.90
Steam required to recover oil from 4,500 lbs. aniline water— 9,000 lbs. @ 50 cents	4.50
Loss of aniline in aniline water, 4,500 @ 0.3 percent = 13.5 lbs.	2.03
Total apparent loss per 1,000 pounds aniline oil	$10 26

Method III. Steam Distillation and Nitrobenzene Extraction of Aniline Waters

The procedure in this system is identical to the previous up to the point where the aniline oil is drawn off from the settlings tanks. Now, however, instead of putting the water through the water stills it is treated with nitrobenzene which extracts the residual aniline from it. Two extractions are made on each batch of aniline water with nitrobenzene that is to be delivered to the reducer house. After the double extraction, the water

which is practically free of both aniline and nitrobenzene is run into a ditch. This process is covered by a German patent. In practice slight modifications to the procedure as outlined in the patent claims are necessary, but on the whole the principle of double extraction works quite satisfactorily.

The patent literature and flow sheet of actual operations follow:

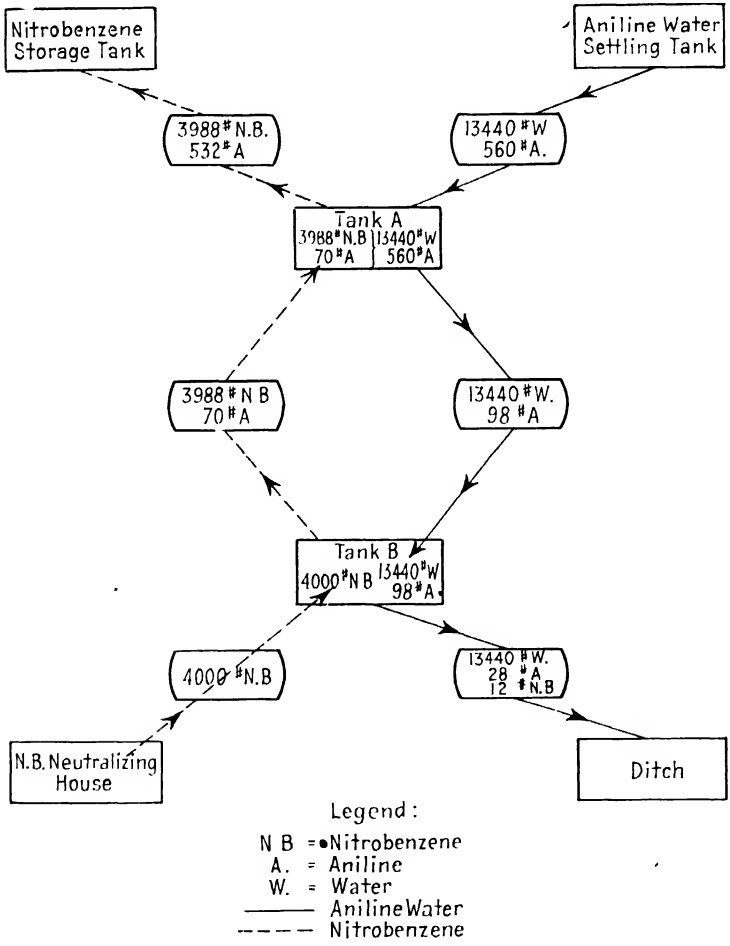


FIG. 11.
Flow Sheet. Nitrobenzene Extraction of Aniline.

Process for the Extraction of Reduction Products of Aromatic Nitro Bodies from Aqueous Solutions *

" Reduction products of aromatic nitro bodies, such as aniline, toluidine, xylidine or the like, are treated with steam after the reduction is completed. In addition to the oily liquid, an aqueous distillate, which is saturated with the reduction product, is obtained. Thus one obtains, in the treatment of aniline or azobenzene with steam, a more or less large mass of distillation water which is saturated with aniline or azobenzene, in addition to the oily distillate of aniline or azobenzene. In a well-conducted operation one is compelled to work up this distillation water again and use it, as a feed for the steam boiler which produces the steam for the distillation of the aniline, etc.

" It has been observed that the extraction of these compounds from the distillation water can be done very simply and quite inexpensively if it is agitated with the corresponding nitro compounds such as nitrobenzene, or nitrotoluene. Here the aniline or the azobenzene, dissolved in the water, is absorbed almost quantitatively by the nitro products. By distillation a quantitative separation takes place in the nitrobenzene and aniline. In the large operations it is the customary practice that the extract (for example the nitrobenzene with the dissolved aniline) be put back into the reducer to be again worked up. It is clear that this process must work very economically where the expensive and time-consuming fractional distillation (in aniline water stills) is eliminated.

" It is generally known that one can extract with ether, benzene, ligroin, etc., amino bases which have been dissolved in water; in the literature no reference has been made to the fact that the original nitrobenzene can be used for the extraction of the amino compounds.

" The extraction with ether, benzene, etc., demands a bothersome apparatus for a large production and the volatility of

* German Patent No. 282,531. Application October 15, 1914. Granted February 1, 1915.

this means of extraction leads necessarily to losses. On the other hand there is NO LOSS in the use of nitro bodies due to their great volatility.

EXAMPLE

"2,000 parts of water saturated with aniline are stirred with 2,000 parts nitrobenzene in an agitator until the nitrobenzene can absorb no more aniline. Then let it settle. Transfer the lower layer 'A' which contains the nitrobenzene into a second container, while the watery layer remains in the agitator, in order that it may again be stirred thoroughly or extracted with fresh nitrobenzene. The water is then almost free of aniline, it is syphoned off or removed, while the nitrobenzene 'B' is left in the vessel and serves as an agitator for the new mass of aniline water.

"The nitrobenzene obtained first, which has absorbed the chief mass (about 57 kg.) of aniline, is fed to the reducer in order to work off the aniline."

In practice we find that 5,990 lbs. of aniline water accumulates per 1,000 lbs. of aniline made, using non-jacketed reducers. In order to treat all this water with nitrobenzene a ratio of 5 : 1 will have to be used as this is the ratio of water production to nitrobenzene reduced. When aniline water is thus extracted the following separation cost is incurred.

Cost to steam distill (see previous)	$3.00
Reducer sludge—identical to previous	1.11
5,990 lbs. H_2O @ 0.25 percent nitrobenzene loss = 15 lbs.	.90
5,990 lbs. H_2O @ 0.35 percent aniline loss = 21 lbs.	3.15
Total apparent loss per 1,000 lbs. aniline..	$8.16

Method IV. Steam Distillation of Aniline

NITROBENZENE EXTRACTION JACKETED REDUCERS

If jacketed reducers are used a smaller volume of water would consequently have to be handled. The results show a distinct improvement as a 10 : 3 ratio for extraction is used.

Cost to steam distill aniline in jacketed reducer	$3.00
Sludge—6 lbs. @ 15 cents	.90
4,500 H_2O @ 0.25 percent nitrobenzene — 11.2 lbs.	.67
4,500 H_2O @ 0.25 percent aniline — 11.2 lbs.	1.68
Total apparent cost per 1000 lbs. Aniline	$6.25

The extraction method of treating the aniline water necessitates a number of large tanks, and in general is a cumbersome method. It may be conducive to getting large quantities of water in the nitrobenzene scale tanks and consequently seriously affect the reduction operation. **The principle of nitrobenzene extraction may however be very successfully applied where only small quantities of water are involved, as in the residual aniline water in the syphon system.**

Method V. Aniline Boiler Method

The practice of using the surplus aniline water in a boiler generating steam for use in the reducers is one that has found particular favor in Europe. The operation is indeed quite simple and the reason for its not finding wider appreciation in the past has been due probably to the slight difficulties with boiler tubes. This difficulty should be easily overcome by proper coordination between boiler manufacturers, tube metallurgists, and aniline producers. It is reasonable to believe that the correct type boiler, provided with tubes of proper chemical composition, will give excellent results.

The operation calls for a large aniline water reservoir into which all the aniline water from the settling tanks is delivered. From a side valve considerably up from the bottom of the tank the water is drawn off for delivery to the boiler feed tanks which deliver the aniline water under pressure to the boiler. A leak in any of the tubes can be promptly detected either in the fire box or smoke stack. The steam line from the boiler is led to the reducers and is connected up separately, so that pure steam can be used to complete the reduction and distillation. It is easy to see that the delivery of the aniline water to the boiler is a very simple and inexpensive way of handling it. The re-

ducer charge *must be neutralized,* however, to minimize boiler tube troubles.

There is no loss by dumping aniline water still residues and the cost of generating steam here should not be much greater than that generated at a distant central power plant.

The apparent sources of loss are:

Cost to distill 5,990 lbs. H_2O from non-jacketed reducers *@* \$0.50 per 1,000 lbs. steam	\$3.00
3,700 lbs. sludge *@* 0.2 percent aniline = 7.4 lbs.	1.11
Cost of separation	\$4.11

Method VI. Jacket Reduction and Vacuum Still

This system is quite new. It involves the use of a large cast iron vacuum still into which the whole charge from the reducer is dropped by gravity. As soon as the charge is in the still the entry valve is closed and the distillation begun. Inasmuch as the distillation is carried on in vacuo, the aniline water comes over first, and the mixture continues with increasing proportion of aniline until all the water is out. The aniline content is over half distilled by the time water-free aniline distills over. This fraction continues only a short time when the oil is darkened by contamination with the residual sludge.

The equipment in this system consists usually of large 1,500 gal. reducers capable of holding 5,000 lb. charges of nitrobenzene. Above the reducer is placed a baffle box to hold back any solid particles. By steam connections the baffle box is flushed clean, back into the reducer. The gas after leaving the baffle box goes through a large condenser, at the base of which are connections returning the liquid back to the reducers.

The reducer can be fed by putting in the complete charge of nitrobenzene along with one-third of the ferrous chloride and a heel of aniline water from previous charges. The iron is added frequently in small batches until the feeding is completed.

The reduction is affected by putting about 25 lbs. steam pressure on the jacket and maintaining the agitation until the reflux from the condenser indicates that the charge is completely reduced.

The drying still is now put under a slight vacuum and the charge dumped into it from the reducer. At first the distillate is very cloudy, but this clears up after the charge settles down in the still. In about an hour the steam is turned into the jacket of the still and the distillation carried on as rapidly as possible. During the first part of the distillation the aniline is contaminated with water. The last 15 percent of the aniline is quite dark due to contamination with sludge.

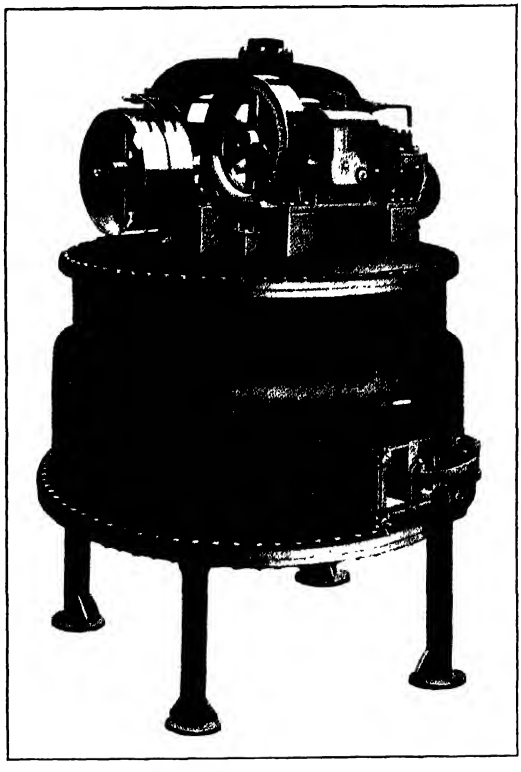


FIG. 12.
Heavy Duty Still (Jacketed).
For distilling reducer charges in vacuo.

This system would work very satisfactorily if it were possible to reduce the aniline content of the sludge in the still to about one half of one percent, during the period that the reducer was

preparing another charge. It would then be possible to double the productivity of each reducer. However, in view of the fact that the vacuum still is so costly the saving is more apparent than real.

In practice the operation of the vacuum still is not all that could be desired, as the load on the stirring mechanism during the stage where only about 10 percent oil remains, is enormous, and considerable power is needed to drive the machinery. When the distillate slackens down to a point where very little aniline is coming over, the vacuum on the still is released and the dumping door opened to discharge the dry sludge into industrial cars for that purpose.

An analysis of this sludge which is very fine shows that it is practically all magnetic iron oxide. As it is hot, the surface material sets up an oxidation to the red Fe_2O_3. The aniline determination on the sludge shows that unless rather long periods (18 to 24 hours) are allowed for drying, considerable aniline remains.

The vacuum distillation system apparently doubles the productivity of the reducers. There is no accumulation of aniline water; in fact there is a slight deficiency as about one part of water to one part of aniline made is used in feeding the reducer. The water dissolved in the aniline must be made up by the addition of fresh water. If equal parts of water and aniline are present in the still, about three parts of steam will be used to distill in vacuo the two parts of aniline and water combined. During the first part of the distillation the ratio between steam used to aniline water distilled will be 1 : 1 and even less during the pure aniline phase. During the latter part of the distillation there is quite a large consumption of steam with very little aniline oil distilling over; the heat being expended in order to raise the temperature of the iron oxide. An analysis of separation costs per 1,000 lbs. of aniline:

Sludge—2,000 lbs. @ 0.5 percent oil = 10 lbs. @ 15 cents	$1.50
Steam—3,000 lbs. @ 50 cents per thousand lbs.	1.50
Total apparent cost per 1000 lbs.	$3.00

The above chart calls for a reduction of aniline content to

½ of one percent. In the above process considerable reducer time would have to be lost waiting for stills, in order to get it down to that point. Again a considerable increase in power costs accrues from operating the very cumbersome stills. The amount of water for condensing purposes is however slightly less than that consumed by distillation methods of separating the oil. It is evident that the system is quite closed and that the material is subjected to comparatively little handling. During the distillation the various aniline fractions are distributed in specified tanks supplied with sight glasses, thus facilitating delivery of aniline to the rectification house and return of water to the feed tanks.

A modification of the preceding vacuum still method is however operated with apparently great success. Instead of dropping the reducer charge into an agitated vacuum still it is dumped into a large horizontal vacuum tank, supplied with a large number of horizontal, welded, extra heavy, steam coils. Heat is applied as before and the distillation goes on even more rapidly than in the agitated still due to the greater heating surface used. At the close of the distillation the manhead to the vacuum tank is removed and the dry sludge is flushed out at the base. This still is able to distill out the oil in approximately the same time required for a reduction and is consequently quite successful in making for efficient operation. The yields (nitrobenzene to aniline) obtained by the manufacturer using this system run consistently over 70 due to the slight handling of the material.

Method VII. Filtration Method

In this system the entire charge from the reducer is drawn on to a large filter press. The sludge is washed several times with aniline water and dried with steam or warm air. The sludge is dumped, containing about 0.3 percent residual aniline.

DISCUSSION

This scheme of removing sludge from the reducer charge is used universally in the manufacture of paraphenylene diamine where paranitroaniline is reduced by the use of iron bor-

ings and hydrochloric acid. The sludge in this process is identical in physical and chemical properties to the by-product from the nitrobenzene reduction. However, three noticeable differences must be taken cognizance of. First, that paraphenylenediamine is soluble in water, secondly that aniline is made in immensely larger quantities and finally the margin of profit on the more costly phenylenediamine in considerably greater than obtained from aniline. In view of these facts it is necessary not to cause any undue dilution or accumulation of aniline water in washing the sludge and, furthermore, it is imperative that a rapid method of getting rid of the cake from the press be provided.

In experimental runs no difficulty was experienced in removing the sludge from the press and after a number of runs the filter cloths were all in good condition. The sludge did not harden or cake, and a few quick blasts with air or steam through the leaves, followed by the tapping of a large wooden mallet, was sufficient to cause the iron oxide to drop off as a fine dry powder.

The sludge can be washed with hot water and then dried with air or steam. Such methods leave about 2 percent aniline in the sludge and maintain a water balance (*i.e.*, do not accumulate excessive water). However, if the washings are kept in a reservoir and pumped through the press immediately after filtration, the cake then is wet, only with water of about 5 percent strength instead of the original 50 percent mixture. If this is then steamed for a few minutes the strength of the aniline water is only about 3 percent. In order to eliminate the possibility of any accumulation of water occurring in the filtration system the following schemes can be used:

I. Use of aniline water to wash leaves of the press, following by a short period of steaming.

II. Use of air instead of steam in forcing reducer charge into press. This will eliminate a large quantity of water that is introduced at this phase of the operation.

The reducer charge contains approximately two parts solids to one part of aniline and water each, at the close of reduction.

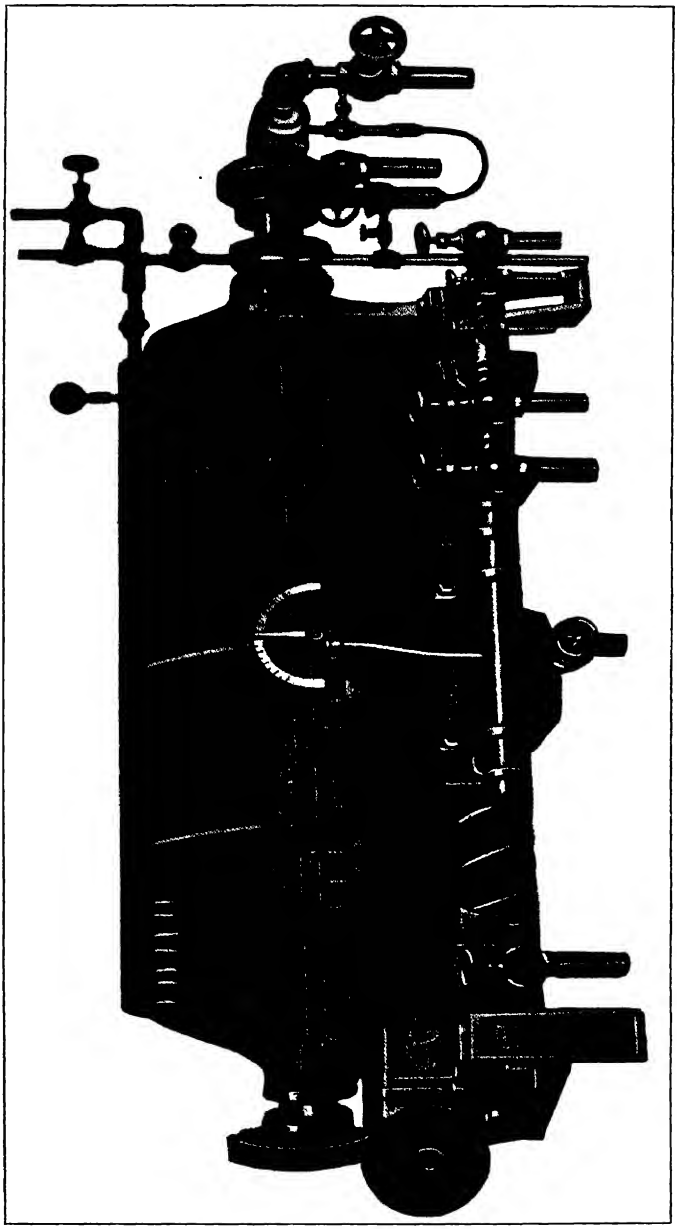


FIG. 13.
Vallez Filter.
Showing screw conveyor for dumping sludge. The filtering leaves are attached to a rotating shaft insuring an even thickness of the cake.

The sludge on the leaf, therefore, is wet originally with a 50 percent mixture of aniline and water. After washing with aniline water, the 50 percent mixture is replaced with a 5 percent solution, only one-tenth of the aniline remaining. The percentage of liquid on the leaves is 8 percent. In terms of 1,000 lbs. of aniline produced, 2,000 lbs. of sludge contain 160 lbs. of liquid containing 5 percent of oil, thus involving a loss of 8 pounds of aniline. This strength and moisture content can be reduced by resorting to the manipulation previously suggested.

The separation costs by the filtration method are then:

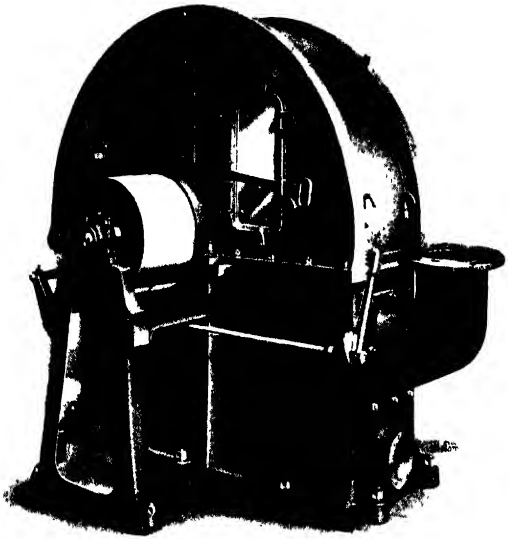
Loss of aniline in sludge, 8 lbs.	$1.20
Extra power cost	None

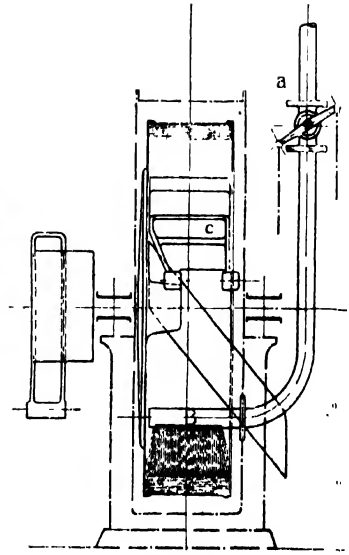
Some of the advantages of filtration separation are:

Simplicity of operation
Low operating cost
Doubly productive capacity of reducers
Losses from treatment of aniline water or steam charges in distilling out aniline from reducer are eliminated
Elimination of an immense quantity of cooling water
Compact system making for good yields

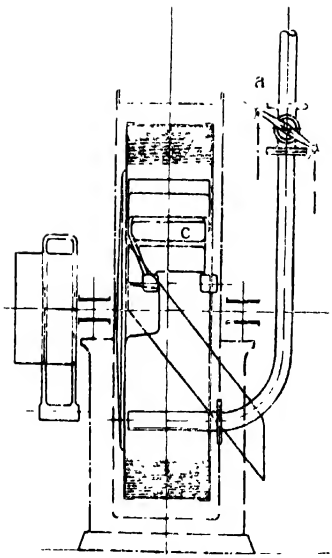
The selection of filter cloths will unquestionably be a very important problem. A cloth that is too fine will make the filtering operation quite difficult. A coarse metal cloth will work quite satisfactorily but permits of considerable fine sludge going through the leaves. This handicap can be overcome by the use of properly designed settling tanks and by the introduction of a secondary filtering device. This additional filtering medium divides the load so that the operation at each point runs easier. However, the second filtering medium needs to be quite simple, and free from difficult manipulation.

The use of either a Vallez filter or of a Haubold self-dumping filter would appear to make a simple and satisfactory installation, as both these machines are capable of making a rapid disposition of the sludge after it is washed.

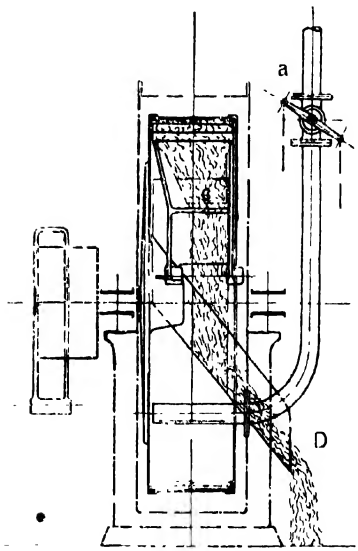




Charging



Centrifuging



Discharging

FIG. 14.
Haubold Automatic Self-Unloading Rotary Pressure Filter.

Method VIII. Syphon Separation

The introduction of a syphon into the reducer at the completion of the reduction stage to draw off the supernatant oil from the watery layer below is a novel and inexpensive method of carrying out the separation. A glance at the specific gravity table shows that above 160° F. the aniline oil layer becomes lighter than the aqueous layer and rises to the top. This separation is accelerated and made sharper by the addition of salt, the salt going into solution in the water, thus further raising its specific gravity.

Jacketed reducers are used in this system and the reduction of the charge is brought about by the application of steam through the jacket. Owing to the fact that there is a slight loss of moisture during jacket reduction it is necessary to have the batch quite fluid during the feeding operation. A 2 to 1 ratio of water fed in to aniline produced gives satisfactory results. In practice, if a larger quantity of water is fed in more steam will be required to eliminate the final aniline after the top layer of oil has been syphoned off. The larger water ratio within certain limits makes the operation run more smoothly by preventing the sticking of machines. Too great a water content, however, slows up the reduction.

The syphon is an inverted funnel operating by a hand worm drive through a tight stuffing box. During the operation the syphon is worked up towards the top of the reducer so as to be out of the way of the paddles.

One of the manufacturers using this process makes use of a bent tube for syphoning out the oil. The 2 inch tube penetrates the side of the reducer through a stuffing box above the jacket line and an improvised gauge on the outside of the reducer indicates the position of the bend inside. By this means it is possible to lower the bend quite accurately to any depth and later to raise it out of the sphere of agitation. This scheme avoids almost completely stoppage in the draw-off line and breaking off of the syphon; which difficulties are encountered when the syphon is suspended from the top cover of the reducer.

When the reduction is just completed, the charge is neutralized with 40 lbs. of lime per 1,000 lbs. aniline separated and 5–10 percent (compared with nitrobenzene used) salt is added and agitation continued until the salt is completely dissolved. Then agitation is stopped, the agitator blades are raised above the sludge and the charge settled. Steam is kept on the jacket to maintain a temperature of 85°-90° C. in the reducer. At this temperature the aniline will rise to the top of the charge. The saline aqueous layer will be underneath, while at the base the sludge will settle out. The introduction of filter-cel along with salt has been suggested for expediting the separation of the layers and effecting a more thorough clarification of the aniline layer.

After settling about one hour a slight vacuum is put on the aniline tank which is to receive the charge from the reducer. The syphon line which delivers the aniline from the reducer to the receiver is now opened and the syphon lowered by the operating mechanism into the reducer. A sight glass on the delivery line indicates the rate of delivery and the quality of the aniline. If too great a vacuum is used considerable turbidity results. The syphon is slowly lowered until the sight glass indicates that the aniline is being contaminated with considerable water.

The remainder of the charge consists of aniline water and iron oxide sludge. With the agitation on, the aniline is then steam distilled until the distillate shows that the charge is free of aniline. The charge is then dumped. This final distillation may be made in a separate still if production requirements justify such an installation.

In view of the fact that very little oil is left after the syphon operation, the distillation consumes very little time and not considerable steam. In fact most of residual aniline water can be used for the final wash of the nitrobenzene in the neutralizing tub (see page 71), and thus save the expense of steam distillation.

If the reducer charge contained 4,000 lbs. nitrobenzene, about 3,000 lbs. of aniline would be in the reducer. The 6,000 lbs. of water used in the feeding contains now approximately 10 percent of aniline, or 600 lbs. of oil. To steam-distill this

would require about 5,000 lbs. of steam. It is thus evident that there will be a deficiency of feed water for the next charge.

The cost of separation per 1,000 lbs. of aniline by this method would then be:

Salt—250 lbs. @ 1 cent	$2.50
Steam—1,700 lbs. @ .50/ 1,000 lbs.	.85
Sludge water—2,000 lbs. @ 0.3 percent = 6 lbs.	.90
Total cost of separation	$4.25

The syphon system is indeed very attractive as it lends itself to adaptation to any existing plant. It is very compact, as there is no aniline water problem. The distillate obtained in clearing the reducer charge of aniline is collected in separate water tanks. The aniline that has settled out is drawn off and added to the oil syphoned off. The cost of the salt (the use of which may be dispensed with and yet obtain satisfactory separations) is practically negligible when compared to the cost of steam necessary for distilling four-fifths of the aniline from the charge.

A filter box similar to that recommended for the filtration system can be used to advantage in order to eliminate the fine sludge that is drawn over with the aniline. These boxes are so constructed that they can be opened and cleaned in a few minutes, and if necessary the used filter plate can be removed and replaced by sliding in a new one. If such a box is not interposed in the system, it is advisable to filter the oil through a pressure-filter before rectifying.

The cost of installation and maintenance is very low. When using the syphon system there is less machinery used than in any of the other systems. There is also comparatively little handling of the oil and consequently the yields are considerably higher than in those systems where aniline water is accumulated and has to be treated.

Owing to the fact that the sludge has to settle out to effect a satisfactory separation, a mechanical problem is presented in providing a proper type of transmission to enable starting up of the machines after the separation, in order to distill out the resid-

ual aniline and to dump the charge. As a rule if fine iron borings is used and fed in small batches, the resulting sludge will not give any trouble. In fact in some reduction plants (P. Phenylenediamine mfg.) it is a practice to let the reduction charge stand over night, when only one shift is working. But this mechanical problem is not serious and observation of the above two precautions should give excellent results without resorting to unusual expenditures for changes from standard type transmission. When the agitators can be raised during the settling period no trouble is experienced in restarting.

DATA CHART

Syphon Method of Aniline Preparation

Charge No				Reducer					Date	
	Time			Materials Used					Depth in Inches	
Operation	Start	End	Elapsed	N B	Acid	Iron	Soda Ash	Salt	4 ft Tank	Reducer
Starting	2:30	3.15	¼	2,500	180	100				
Water Added									25″ or	1,680
Steam Added										Live
Reducing	3 15	9 15	6 00			2,600				
Finishing	9 15	10 30	1¼							
Steam Added										
Neutralizing	10.30	11:00	½				80			
Laying Down	11.00	11.30	½					500		
Settling	11 30	12 30	1 hr.							
Depth										51″
Skimming									Brine	8″
Depth									Oil	9″
Steaming	1 30	5 30	4 hrs							
Steam Added										
Distillate										
Dumping	5:30	5.15	¼							
Total	2 30	5 15	15¼	2,500	180	3,000	80	500	25	

The sludge in the scheme just outlined is of course wet. This can be dumped dry if market conditions justify such a procedure. To accomplish this the reducer charge is dumped immediately after close of reduction into a vacuum still, similar to that used in the vacuum still process. Here the charge is settled and the oil syphoned out. The aniline water is then distilled out under atmospheric pressure, with jacket steam.

When the oil is completely off, the water vapors are distilled out doors, until the sludge is dry. It is then dumped into a truck for removal to the cooling grounds and kept under cover until the oxidation reaction is complete. To get the sludge dry, therefore, entails the introduction of considerable new machinery and the consumption of 2,000 lbs. steam per ton of dry sludge. It is questionable whether the market would justify this expense when using the syphon system.

The above chart records an actual run in one of the large plants using the syphon system.

Conclusions Based on Review of Processes

It would be quite indefensible to draw conclusions from the preceding tables of losses only. Many other factors enter into the making of an efficient plant besides the tabulation of comparative sources of loss and increased power charges necessary to obtain the material desired. However, it is well to summarize the findings obtained thus far and endeavor to draw conclusions based on the actual or feasible operations of each scheme.

The apparent comparative demerits for separating the crude aniline from the reducer charge are as follows:

Type of Separation	Cost per 1000 lbs Aniline
I. Steam distillation of aniline non-jacketed reducer	$12.81
II. Steam distillation of aniline in jacketed reducer	10.26
III. Steam distillation of aniline—nitrobenzene extraction of aniline water—non jacketed reducers	8.16
IV. Steam distillation of aniline—nitrobenzene extraction of aniline water jacketed reducers	6.15
V. Use of aniline boiler to generate steam from aniline water	4.11
VI. Jacket reduction accompanied by vacuum still	3.11
VII. Filtration of reducer charges. Shows large savings in power	1.20
VIII. Syphon separation according to modifications	1.00 to 4.25

It is safe to assume that the first four methods are quite antiquated. With the introduction of special and highly efficient types of machinery the separation of aniline oil from the reducer charge by means of steam distillation must be considered entirely inefficient. The principle of nitrobenzene extraction, how-

ever, may be found applicable towards working up the residual aniline water and sludge when using the syphon system. Such an adaptation if worked out successfully would so enhance the value of the latter process as to give it an unquestioned superiority. Only when a well-designed boiler is used to take care of the excess aniline water can the distillation method compete at all with other existing systems. As was pointed out previously such an aniline boiler must needs stand up with little tube replacement. At times the aniline content in the water varies considerably and it is apparent that the aniline boiler will be called upon to work up solutions of high concentration. When the boiler is used, the precaution of neutralizing the reducer charge must be strictly observed, not so much as a problem of increased yields, as one of reducing boiler troubles. The installation and supervision of a separate steam-producing unit is of course one of the drawbacks to the system.

Vacuum distillation of the reducer charge is at present being accomplished either in a heavy duty, agitated jacketed still, or in a horizontal vacuum tank in which specially designed steam coils are placed. It is quite apparent that the separating charges are comparatively smaller and that the reducers are free for a greater number of charges than in other methods. The horizontal still of course reduces electric power costs and the maintenance of expensive extra duty stills. However, it is necessary to waste the oxide sludge from the former, and if there is a market for that product the apparent advantage is almost counterbalanced.

The separation by use of a large filter press designed to make disposal of the sludge easy is almost an ideal method of handling the charge. The cost of installing presses capable of holding 5,000 to 8,000 lbs. of sludge is considerable. A certain amount of work may be expected in cleaning and maintaining the presses in good order. Thus far this method has only been tried on a small scale, and the results obtained augured for very efficient plant operation. The change from present methods of operation to the filtration of the entire charge is quite daring and is yet to

be developed on a large scale. As suggested previously the use of either the Vallez filter or Haubold automatic self-dumping filter may solve this problem quite satisfactorily.

The syphon system of separating the oil is used by several of the smaller producers with great success. The cost of the salt for accelerating the separation is the largest item of expense in effecting the removal of the aniline oil. If this cost were not included in the comparative tables it would make a much better impression. When compared with the vacuum still method which is regarded as its closest competitor, the former method requires no costly installation of stills, can operate with a smaller steam plant, and consumes much less water and electric power. The layout of the syphon plant is much simpler and requires less operating expense to keep it in good condition. The yields obtained by the syphon system would appear to be greater than those that can be expected from the vacuum still, as it is very difficult to remove the last 1 percent of aniline from the sludge when evaporating to dryness. Finally the steam cost for recovering the aniline from the residual water may be eliminated by treating the water with nitrobenzene next to be reduced, or using it as a wash water in the nitrobenzene operation.

Bearing in mind the criteria to be observed in the selection of a process for separating the aniline oil from the reducer sludge charge one will not be far amiss by adopting the reverse order of presentation as an expression of comparative efficiency.

CHAPTER V

FERROUS CHLORIDE AS A REDUCING AGENT

In 1916 there appeared in Friedlander (Vol. XII, page 3) an article by Drs. Conway and Girsewald, entitled "Reduction of Nitrobenzol to Aniline with Metallic Iron and Water using Ferrous Chloride as a Catalyzer." The patent is granted at Berlin, November 9, 1914.

According to Hugh S. Taylor, an eminent authority on the subject of catalysts, there exists a class of catalysts known as the cyclic catalysts. This class consists of compounds which change their form during the promotion of the reaction, but which are regenerated in their original quantity at the close of the reaction. To quote Dr. Taylor, "The participation of the catalyst as an intermediate compound in the cycle of operations is not excluded, but a true catalytic agent must be regenerated in its original chemical form on the completion of the cycle."

It is thus apparent from a review of the formulæ suggested as underlying the reduction process that ferrous chloride is a true catalyst of the cyclic class, inasmuch as it is regenerated in its original form at the end of the cycle.

$$\text{I. } C_6H_5NO_2 + 2Fe + 4H_2O = C_6H_5NH_2 + 2Fe(OH)_3$$

$$\text{II. } 2C_6H_5NH_2 + FeCl_2 + 2H_2O \quad 2C_6H_5NH_2 \cdot HCl + Fe(OH)_2$$

$$\text{III. } 2C_6H_5NH_2 \cdot HCl + 2Fe(OH)_2 + 2Fe \quad 2C_6H_5NH_2 + FeCl_2 + Fe_3O_4 + 2H_2$$

Since the ferrous chloride is regenerated in its original form and quantity at the completion of the cycle through which it passes in the conversion of the nitro body to an amine, it follows that this method of reduction is a catalytic reaction.

The substitution of a neutral reagent for the hydrochloric acid commonly used in the manufacture of aniline oil and other amines was a notable achievement. Its introduction into technical reduction processes marked great progress not only in more efficient operation, but permitted of a more sanitary environment

for the reducer operator. This transition has meant the elimination of costly acid tubs and lines, and its accompanying disagreeable features. It has resulted largely in the scrapping of lead-lined and hard rubber equipment incidental to technical reduction processes on a large scale. This change in procedure has also increased the life of the reduction apparatus; has improved operating conditions and has effected a lowering of costs in the manufacture of aniline.

The use of ferrous chloride as a catalyst, of course, simplifies the actual work of feeding the reducers, as this material can be fed in along with the iron, or dumped in like the iron borings at specified intervals. The amount for each charge is weighed out and brought to the reducer. Some operators prefer to add the whole batch of crystals directly at the start of operations along with the entire charge of nitrobenzene, whereas others divide the feeding of the chloride into two or three installments. When all the chloride is added at once there is a tendency to form excessive pressures after the initial reaction sets in, and consequently is not as safe as the method of intermittent feeding of the chloride.

Ferrous chloride can be purchased in crystal form or as powdered anhydrous material. The specifications for the crystals are as follows:

Ferrous chloride content—not less than 58%
Acidity as HCl—not more than 0.25%

The oxidation of ferrous chloride in the air results in a small percentage of ferric chloride being present. This, however, is not objectionable as it is immediately converted to the ferrous state in the presence of free, finely divided iron in the reducer. A minimum of acidity is, however, desired, as its presence would defeat the purpose of a neutral reduction.

The cost of ferrous chloride used in the reduction as compared with hydrochloric acid consumed is for all practical purposes identical. The consumption of ferrous chloride crystals being exactly one-half by weight of 30 percent HCl used. As the market price of the salt has been just about double the price

of the acid, the material cost is thus equal in both cases. The real saving when using crystals is realized, however, in the minimized repair and maintenance charges.

A condensed operating report showing actual plant practice reveals the following data; the aniline in the case being steam-distilled into a receiver after the reduction was complete.

Reducer No. 1

Nitro Benzene Used	Iron Borings Used	$FeCl_2$ Crystals Used	Actual $FeCl_2$	Time in Hours to		
				Feed	Reduce	Distill
1,100 lbs.	1,100 lbs.	53 lbs.	30 lbs.	3	3	6½
1,100 "	1,230 "	53 "	30 "	3	3	6½
1,100 "	1,100 "	53 "	30 "	3	3	6½
1,100 "	1,230 "	53 "	30 "	3	3	6½

Reducer No. 2

1,100 lbs.	1,100 lbs.	53 lbs.	30 lbs.	3	2¼	6¼
1,100 "	1,295 "	43 "	25 "	3	3¼	6¼
1,100 "	1,230 "	43+10 "	25+5 "	3	4	6½
1,100 "	1,100 "	53 "	30 "	3	3	7

Reducer No. 3

1,100 lbs.	1,100 lbs.	53 lbs	30 lbs.	3	3	6½
1,100 "	1,230 "	53 "	30 "	3	4	6½
1,100 "	1,100 "	53 "	30 "	3	3	6½
1,100 "	1,165 "	53 "	30 "	3	3	6½

NOTE: The foregoing remarks are to a large extent applicable when aniline salt is used in the reducer to replace the acid.

CHAPTER VI

IRON BORINGS

Preparation on The Plant

A good grade, soft, cast iron turnings gives the best results in the reduction operation. The selection of the borings, however, often resolves itself largely into a matter of checking cost against convenience and quality. Several manufacturers now prepare a technical grade of chemical borings for delivery to the consuming chemical trade which gives very good results. The cost of this quality borings is, however, considerably greater than the rougher turnings which may be purchased from brokers. The chemical iron is very uniform in quality and fineness and is free from grease. It is sold on the short ton basis and delivered in 100 lb. bags.

The iron purchased from brokers is never quite as clean nor as uniform as the former, the shipment being usually a collection of turnings from one or more shops or foundries. Oftentimes a large percentage of a shipment consists of bolts, nuts and other shop refuse. This class of turnings also contains considerable steel which is not effective to any great extent in the reduction operation. This crude material may be delivered in closed box cars or open gondolas. In the latter case a frequent accumulation of large rust lumps results due to exposure. The cost of unloading the open cars is less, however, when handled by steam shovels. At one large plant where crude borings are bought the following method of handling is pursued.

The borings are unloaded from the box cars or gondolas into narrow gauge service cars and delivered into the top of the grinding building.

A Gardener crusher or Sturtevant ring roll mill can be used to reduce the borings to a uniform size suitable for use in the reducers.

The arrangement of the grinding apparatus is as follows: The crude iron borings are shoveled onto a coarse screen (½ in.

mesh) to remove all debris, and large pieces of steel and iron. The borings drop into the boot of a bucket elevator, are lifted up and then discharged onto a 5 mesh shaker screen. The "' fines" drop into a hopper feeding the reducer house service cars. The coarse material drops off at the end of the shaker screen and falls through a closed chute leading into the grinding machine. The outlet from the crusher leads to the elevator boot and the ground iron now goes up with the fresh material. The chute feeding the iron into the crusher is connected with an air jet discharging into a wooden soot box. This device makes it possible to get rid of the very fine particles and to avoid unusual dust in the building. The "fines" are afterwards mixed with some coarser material and used in the reducing machines.

A sieve test on the crude and ground material gives the following results:

Sieve Test

Mesh Screen	% Thru	Crude	Ground
10		54 7	76
20		27.9	40.5
40		11.8	17.5
60		5.2	11.5
100		1.7	7.0

Investigation—Use of Fine Iron Borings

The above ground iron was delivered to the reducers, and in the course of the operation it was evident that a considerable portion of this iron was not acted upon during the reduction. This was apparent by an examination of the residual iron sludge at the operating houses. This sludge was very heavy and had a tendency to set. When crumbled and closely inspected, it was seen that a large percentage of it consisted of small, highly polished, smooth, steel particles. The presence of the steel in the rough iron was, of course, very apparent when putting the borings through the grinder.

From the preceding it is very obvious that the quality of the iron delivered to the plant has a very important bearing on the net efficiency derived from its use. A conservative estimate of the actual iron used from the material received would be 95 per-

cent, the loss of five percent covering the accumulation of nuts, bolts, junk, combustibles, etc., which is screened and delivered to the scrap yard. When gondolas are used for the shipment of iron, an additional loss of 2 percent is expected from large rust lumps which form during transit. As a result of these observations, two samples of "prepared" iron borings were investigated. These were not only finer than the material being used but were also free from the objectionable steel particles which contaminated the plant stock. Some of the plant borings was then specially ground in order to give it the physical properties of the "foreign prepared iron" and a few test runs were made in order to determine what saving in time and material could be effected by its use.

Preparation of Iron

The following table shows the relative fineness of the borings that have been given consideration.

Iron Borings Fineness Test

Through Mesh	Standard Coarse	Special Fine	Prepared Iron No. 1	Prepared Iron No. 2
10	76.0	98.7	92.8	100
20	40.5	70.0	69.6	90
40	17.5	27.8	29.5	49
60	11.5	19.1	11.0	29
100	7.0	11.4	8.0	10

From the above table, it is evident that the "Special Fine" screened through a heavy six (6) mesh wire sieve closely resembled the foreign Prepared Iron No. 1, and was not quite as fine as the Prepared Iron No. 2. The 1.3 percent of iron remaining on the ten mesh screen from the special fine sample is entirely fine, highly polished, steel shot.

Operating Tests

The experiments using the fine iron were carried on in a reducer on which the steam pressure on the jacket and into the

machine was accurately controlled by regulator and pop valve, which assured uniform operating conditions.

The iron hopper above the reducer was thoroughly cleaned of the standard coarse iron before starting operations with the fine material. The following table "A" shows the results of four runs using the standard coarse iron, while table "B" shows the saving of time and materials with the use of the "Special Fine" borings.

"A"—No. 2 Reducer—4,000 lbs. charge N. B.

Using Standard Coarse Iron Borings

	Run No				Average
	7	8	9	10	
Weight of Iron Borings	4,100	4,100	4,550	4,495	4,461
Time—Feed	10 hrs.	10 hrs	10 hrs	10 hrs.	10 hrs.
Time—Reduce	4 "	4¼ "	4½ "	4¼ "	4½ "
Total Time	14 "	14¼ "	14½ "	14¼ "	14½ "

"B"—No. 2 Reducer—4,000 lbs. charge N. B.

Using Special Fine Iron Borings

	Run No				Average
	13	14	15	16	
Weight Iron Borings	4,260	4,000	4,000	4,000	4,065
Time—Feed	8 hrs.	8¼ hrs	8¼ hrs	9¼ hrs	8 hrs 49 min.
Time—Reduce	6 "	4 "	4½ "	4 "	4 hrs 38 min
Total Time	14 "	12¼ "	13¼ "	13¼ "	13 hrs 26 min.

From these tests it can be seen that a saving of 400 lbs. of iron and one hour of time per run can be realized by the use of the finer borings. No unusual difficulty was experienced in feeding this special material, the saving in time being due to the more rapid assimilation of each batch. An analysis of the sludge also reveals an important phase of the reaction. It appears that the finer the iron and the smaller the quantity of material used, the more complete will be the oxidation of the iron.

Coarse Iron Reduction Tests

Following are the operating data on the reduction tests made during the investigation of fine iron borings:

	1	2	3	4
Charge of Nitrobenzene	1,000	4,015	4,000	4,000
Time Started	3 P.M	4 30 A.M.	12 Noon	7:15 P.M.
Initial Feed Complete in	½ hr	½ hr	20 min.	½ hr
Iron all in	10 hrs.	10 hrs	10 hrs.	10 hrs.
Reduction Complete	4 "	4½ "	4¼ "	4 "
Total Time for Feed and Reduction	14 "	14½ "	14¼ "	14 "
Iron Used	4,100	1,550	4,495	4,405
Chloride Used	240	240	240	240

Average iron per charge, 1,162 pounds.
Average time to feed and reduce, 14¼ hours.

Fine Iron Reduction Tests

	1	2	3	4
Charge of Nitrobenzene	1,020	1,000	1,010	4,000
Time Started	12 Noon	1 30 A M	7 15 A M	6 45 P.M.
Initial Feed Complete	15 min	30 min	15 min.	15 min.
Iron all in	8 hrs	8¼ hrs	9¼ hrs	11 hrs.
Reduction Complete	4¼ "	4½ "	4 "	¼ "
Total Time to Feed and Reduce	12¼ "	13¼ "	13¼ "	11¼ "
Iron Used	4,000	1,000	1,000	4,405
Chloride Used	240	240	240	240

Average iron per charge, 1,026 pounds
Average time to feed and reduce, 13 hours.

Sludge Analysis

Metallic Iron	None	None	Trace
Ferrous Iron	11.05%	8.44%	46 81%
Ferric Iron	50.16%	51.47%	13.50%

Cost Considerations

An analysis of the cost of preparing iron borings on the plant compared with the cost of purchasing chemical iron borings shows that it is more economical to maintain a plant grinding equipment provided the daily consumption will average above ten tons of borings per day. The savings based on the above production will be approximately two dollars per ton. This fig-

ure is arrived at after making the necessary adjustments for (1) waste material included in the crude turnings purchased, credit being given only for the relative reducto-active iron as compared with the best standard material obtainable on the open market; (2) for the cost of all factors involved in putting the iron into the reducer houses; and (3) for the standard fixed charges for maintaining such an auxiliary operation.

If the apparent margin of saving were to fall considerably below the above figure, the value of maintaining a plant grinding mill (except for emergency purposes) would be open to discussion, as the borings produced from the heterogenous turnings are seldom as uniform in fineness or in composition as the advertised products obtained on the open market. A good boring will be etched quickly by the action of the boiling acid solution in the reduction kettle and will thus be instrumental in carrying on a steady active reduction without the use of very much supplementary heat. A good iron thus possesses qualities, the positive value of which cannot be readily ascertained, aside from the knowledge that it is free from oil, grit, and combustible material, the presence of which would be deleterious to the most efficient functioning of the operation.

When consideration is given to the reduction of solid nitrocompounds which are usually prepared on a much smaller scale, the cost of the iron borings is usually secondary to obtaining the best quality material. In fact an excess of iron over the quantity known to be sufficient to effect reduction is often used for the purpose of eliminating side reactions, and to curtail the amount of acid used, so as to produce less salt in the reduction mass when the latter is neutralized. Such considerations make for higher yields and better quality material which often more than offset the apparent increased iron cost. For the reduction of aniline, however, no great excess of iron borings over the amount suggested in the cost sheet (see Chap. VIII) is advisable. Here, a ratio of 114 pounds of iron per 100 pounds of nitrobenzene is used as a basis for calculations and for a compound as volatile and active as aniline—no larger ratio appears justified. With a

properly designed stirrer for keeping a thoroughly etched iron in constant suspension, very satisfactory results can be obtained with the above ratio. In fact, it can be observed from the above operating reports that a much lower iron ratio (100 pounds iron to 100 pounds nitrobenzene) has been and is now being used. Undue economy, however, is warned against as side reactions may set in with consequent lowering of yields.

Function of Iron in the Reaction

By an inspection of the reduction formulæ suggested as representing the reduction reaction, it appears that the iron fed into the machine acts as an oxygen carrier. An analysis of the residual sludge reveals that the bulk of the iron is converted to the magnetic iron oxide Fe_3O_4. As a reaction proceeds in aqueous solution only the water-soluble ferrous chloride is potent; the aniline combining with the chlorine molecule while the iron immediately combines with the hydroxyl groups liberated. A glance at the equations following:

$$\text{I}\quad C_6H_5NO_2 + 2Fe + 4H_2O = C_6H_5NH_2 + 2Fe(OH)_3$$
$$\text{II}\quad 2C_6H_5NH_2 + FeCl_2 + 2H_2O = 2C_6H_5NH_2 \cdot HCl + Fe(OH)_2$$
$$\text{III}\quad 2C_6H_5NH_2 \cdot HCl + Fe(OH)_2 + Fe = 2C_6H_5NH_2 + FeCl_2 + Fe_3O_4 + 2H_2$$

shows that new iron is needed as soon as the portion in the reaction tub has performed its task as an oxygen carrier. The new or excess iron assists in the hydrolysis of aniline hydrochloride, and the free acid regenerates ferrous chloride to maintain a reducto-active condition. Confirmation of the preceding explanation is evidenced in plant practice, when an operator fails to put the prescribed quantity of iron into the tub and it is found that the addition of more acid or more heat does not aid in bringing about the reduction. The addition of some iron borings, however, immediately shows its effectiveness by a foaming reaction and a rapid reduction.

As previously noted, the presence of a water-soluble iron is needed to maintain the reaction and it is essential therefore to test the solution before feeding additional nitro-body in order

to insure its presence. From equation II one would expect to obtain no positive test for free iron at this point, as the iron appears to be bound up as sparsely soluble ferrous hydroxide. In fact this is quite true. It has been observed that immediately after feeding considerable nitro-body, no, or only a faint-test for iron can be obtained. When the spot test shows, however, that reduction is complete, the iron test is very distinct. In case it is not so, more iron must be added before introducing additional nitro-compounds. Some operators prefer to use a very fine mesh borings to finish up the reduction. This practice is particularly advisable where the bulk of the borings is not of the best quality, but where a good standard borings is used no special precautions for "finishing" are necessary.

CHAPTER VII

MANUFACTURE OF NITROBENZENE

Outline of Operation

The nitration of benzene is carried out in closed cast iron vessels. The operating control is of necessity quite rigid, as slight deviations from standard practice may result in low yields and also lead to the introduction of the element of danger in the operation.

Two methods of nitration are used:

I. Closed system with paddle or draft tube agitation:
   (*a*) top feed
   (*b*) bottom feed

II. Constant level system with sleeve and propeller agitation, or in a Hough Nitrator.

The operation may be outlined briefly as follows:

The nitration is brought about by adding mixed acid to benzene, controlling the temperature at 75° F. when paddle agitation is used; a considerably higher nitrating temperature—140° F.—is permissible when a more perfect agitation is used. Cycle acid (*i.e.*, waste acid from a previous charge in which some nitrobenzene is still present) is blown into the nitrator in sufficient quantity to cover the bottom paddles. This acid is used for the purpose of hastening the reaction, and as it afterwards dilutes the mixed acid added, it makes for a more uniform temperature and even reaction.*

If cycle acid were not used it would take several hours longer to carry out the nitration owing to the greater difficulty in controlling the temperature. Brine is turned into the coils and about 2,000 lbs. of cycle acid are blown into the nitrator. Then 2,600 lbs. of benzene are pumped from the scale tank after the temperature of the cycle acid reaches 75° F.

* For other advantages of use of cycle acid see under "Nitration with Hough Nitrator."

After the benzene is in and the temperature fixed at 75° F., mixed acid is started into the nitrator. The mixed acid can be fed into the top, or undersurface. When the undersurface feed is used, the acid runs into a lead funnel placed on the agitator just above the top paddle. A lead line leads from the funnel to one of the lowest paddles. Here the lead line makes a loop and goes back to an upper paddle where a distributor is attached at the end of the line. The loop in the lead line is always full and prevents spluttering; as the mixed acid here comes in contact with the weak cycle acid at the lower part of nitrator instead of making direct contact with the benzene when surface feed is used.

During the nitration the temperature is held between 70° and 75° F. by feeding acid slowly with a continuous flow of brine or cooling water through the coils. When all but the last 1,000 lbs. of acid has been added the flow is increased. The rate is governed so that at the close of the acid feed the temperature reaches 100° F. After the mixed acid is all in, the temperature is raised to 140° F. by taking the brine flow off the coils. The whole charge is then run from the nitrator to the settling house.

During the first part of the run the acid must be added only slowly, but as the nitration progresses the mixed acid can be added more rapidly. This rate of feed, however, depends entirely on the temperature as controlled by the brine and efficiency of nitration.

To arrive at the amount of mixed acid to be used per charge, it is necessary to multiply the weight of benzene by the acid factor.

The theoretical ratio is .8077 lb. of HNO_3 per pound C_6H_6. This ratio in plant practice is usually increased to 1.01 times the theoretical or to .8150,

$$\frac{.8150}{\text{Act. } HNO_3 \text{ in 1 lb. of mixed acid}} = \text{factor}$$

An average analysis of the mixed acid used, and of the resultant waste acid, is:

Mixed Acid		Waste Acid
52.50%	H_2SO_4	71.50%
39.50%	HNO_3	.50%
.50%	$HNOSO_4$	.75%
7.50%	H_2O	27.50%

Treatment of Nitrobenzene at Settling House

The settling house is provided with a number of large conical-bottomed lead tanks each capable of holding one charge. The charge from the nitrator is allowed to settle here for about 24 hours when the waste acid is drawn off from the bottom of the lead tanks to a blowcase and delivered to the waste acid settling tanks for additional settling or for treatment with benzene next to be nitrated, which will extract the residual nitrobenzene. The nitrobenzene is then dropped into another blowcase and delivered to the neutralizing house. The neutralizing tub may be either a large, lead, conical-shaped tub containing an air spider used for agitating the charge of nitrobenzene during the washing process, or a standard cast iron kettle similar to a nitrator with sleeve and propeller agitation.

The neutralizing tub is filled with a heel of warm water run in from a hot water tub, and the nitrobenzene is blown into it. The charge is thoroughly agitated, and then allowed to settle. The supernatant acid water is then run off through side outlets into a labyrinth where practically all of the enmeshed nitrobenzene will settle out.

The charge is now given a neutralizing wash followed by a wash with aniline water from the reducer house if any has to be worked up and finally run off at the base of the tub into a blowcase from which it is delivered to the nitrobenzene storage house, where it is again settled and final traces of water removed. This crude nitrobenzene can now be distilled for other uses.

In some plants where the nitrobenzene manufactured is used almost exclusively in the aniline plant, the neutralizing wash is omitted. The nitrobenzene delivered to the reducer houses

is consequently slightly acid. Provided the acidity is kept below one-half of one percent no harmful effects on the equipment are noticeable.

Discussion of Nitrating Acid

An investigation to determine the best composition for the mixed acid to be used gave approximately the following formula:

Total	H_2SO_4,	60%
"	HNO_3,	32%
"	H_2O,	8%

This gives a total acidity of 92 percent and a D.V.S.* of 3.5.

Two series of nitrations were made, one in which the total acidity remained constant and the H_2SO_4 was replaced by HNO_3; and the second in which the D.V.S. was kept constant and the total acidity increased as the H_2SO_4 was replaced with HNO_3.

The results of these nitrations are embodied in the following charts.† In the first series, curves were drawn showing the relation between nitrobenzene, benzene, dinitrobenzene, and nitric acid content of the mixed acid. In the second series the relation between nitrobenzene, benzene, dinitrobenzene and total acidity is plotted.

A consideration of Fig. 15 shows that ratio NB B in relation to HNO_3 in mixed acid is quite smooth. As the HNO_3 is increased, the ratio of nitrobenzene benzene becomes smaller, the amount of nitrobenzene becoming smaller and benzene greater. Since the D.V.S. becomes smaller, as the HNO_3 replaces the H_2SO_4 in the acid, the same curve will represent the relation between the D.V.S. and unnitrated benzene. The lower-

* Dehydrating Value of Sulphuric. Determined by dividing actual H_2SO_4 content by total water present at close of the reaction.

E.g., if mixed acid composition is 60 percent H_2SO_4; 32 percent HNO_3; 8 percent H_2O, then during the nitration reaction one molecule of water per molecule of nitric acid and will be formed $\frac{63}{18} \cdot \frac{32}{x} \cdot x = 9.1$. Thus $9.1 + 8 = 17.1$ lbs = total water. $\frac{60}{17.1} = 3.5$ D.V.S.

† Key: B. = Benzene; N.B. = Nitrobenzene; D.N.B. = Dinitrobenzene.

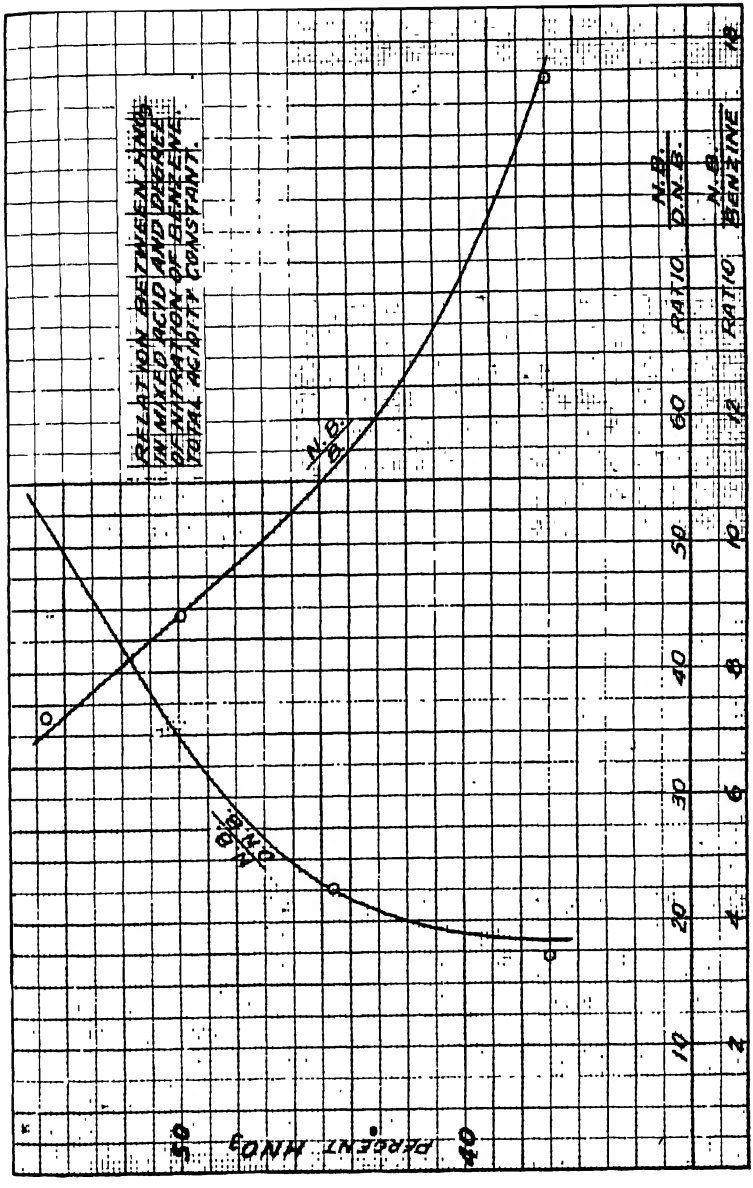


FIG. 15. Nitration of Benzene.

Relation between HNO_3 in mixed acid and degree of nitration of benzene. Total acidity constant.

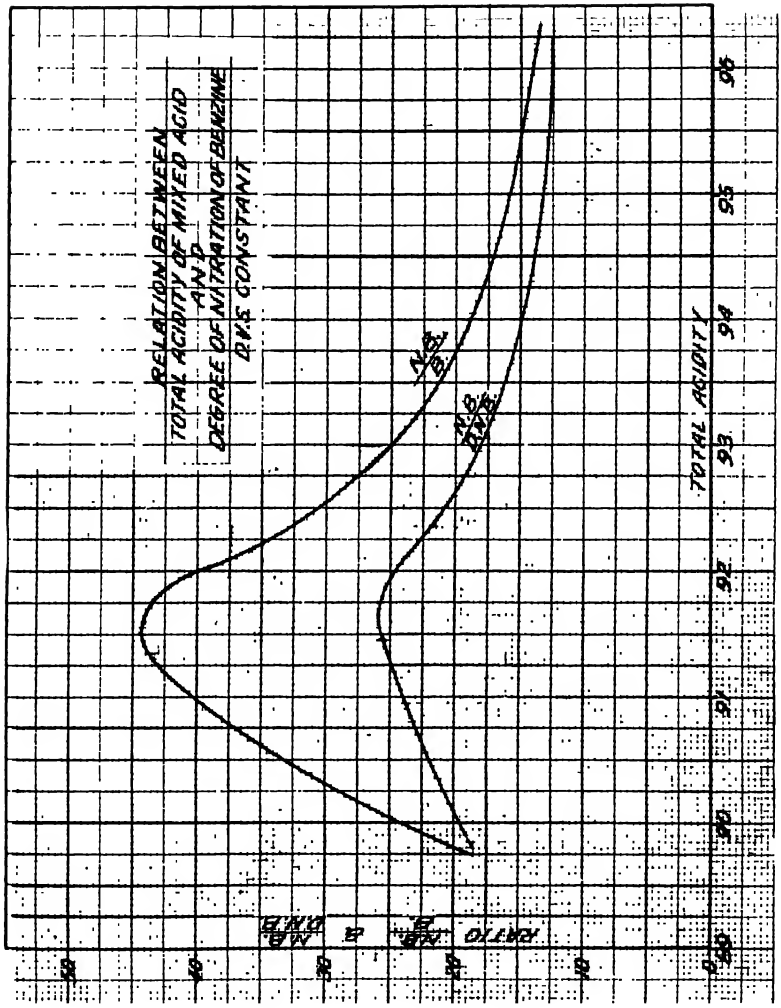


FIG. 16. Nitration of Benzene.

Relation between total acidity of mixed acid and degree of nitration of benzene. D. V. S. constant.

ing of the D.V.S. in this series explains the fact that less benzene is nitrated even though the concentration of the HNO_3 is constantly increasing. It is clear, therefore, that a complete nitration of benzene is not a question so much of percentage HNO_3 as it is of D.V.S. If the amount of unnitrated benzene is to be kept down the D.V.S. must be kept up.

The other curve on Fig. 15 shows that as the HNO_3 replaces H_2SO_4 the ratio Nitrobenzene/Dinitrobenzene changes only slightly up to 45 percent, but then becomes smaller. The dinitrobenzene figures in the tests made varied considerably, but it is evident that not much, if any, increase in D.N.B. is caused by going from a 2.5 D.V.S. (45 percent HNO_3) to a 3.25 D.V.S. (38 percent HNO_3) or even higher to a 3.5 D.V.S. From a standpoint of D.N.B. formation a low D.V.S. would no doubt be advisable but this would unquestionably result in large amounts of unnitrated benzene, and is therefore to be avoided.

Curve Fig. 16 shows the effect of H_2SO_4 reduction under a constant D.V.S. obtained by increases in total acidity. On this sheet the total acidity increased as the H_2SO_4 diminished, the D.V.S. used being 3.5 throughout. At about 92 percent total acidity the ratio of NB/B and NB/D.N.B. seems to be greatest, and both above and below that acidity the diminution is quite marked. It is rather surprising that increased total acidity above 92 percent should cause less efficient nitration of benzene to nitrobenzene but such is evidently the case. The fact that the ratio NB/D.N.B. becomes greater going from 90–92 percent acidity is explained by the fact that the value for NB becomes much greater and not necessarily that the value for D.N.B. becomes smaller. The values for D.N.B. at this D.V.S. (3.5) and total acidity at 90–92 percent are no greater than those obtained with a D.V.S. of 3.25 or 2.5, with similar total acidities. This confirms the statement as regards the effect of D.V.S. on D.N.B. formation as found from curve Fig. 15. With a total acidity at 92 percent and a D.V.S. at 3.5 the necessary acid composition is:

60 percent H_2SO_4
32 percent HNO_3
8 percent H_2O

This acid gives very satisfactory nitrating results, whereas a mixed acid having the composition

$$\left.\begin{array}{r} 52\text{–}54 \text{ percent } H_2SO_4 \\ 38 \text{ percent } HNO_3 \\ 7\text{–}\ 8 \text{ percent } H_2O \end{array}\right\} \text{D.V.S. } 2.95$$

often showed the presence of considerable unnitrated benzene. The composition of the second acid permitted the nitration of larger quantities of benzene with less waste sulphuric acid to be recovered, but owing to its lower D.V.S. it is open to the charge that nitration efficiencies are apt to be lower.

NITROBENZENE OPERATING PRACTICE

Investigation of Procedure

To Analyze

(1) Sources of loss.
(2) Comparative nitrating efficiency of top speed *vs.* under-surface feed.

An attempt is here made to establish a background for benzene nitration revealing any deficiencies and from these fundamentals to follow the improvements made in nitrating equipment and the advances recorded in operating technique.

Fundamental Nitration Conditions on the Plant

The apparatus used for the nitration of benzene consists of a large closed nitrator vessel (which may be placed on a platform scale) with eight banks of brine coils extending around the inside to a point about one foot from the bottom of the vessel. In order to offset the dead space in the bottom of the nitrator which is not provided with refrigeration, enough spent acid is added to bring the lower layer of benzene up to the brine coils.

The agitation is double action, consisting of two vertical shafts, rotating in opposite directions, the top blades of which are so pitched as to beat downward, while those at the bottom

contribute an upward motion to bring about an intimate mixing of acid and benzene.

The fume recovery apparatus attached to the nitrator consists of a lead exit pipe leading from the nitrator to a Woulf bottle placed upon the floor. Upon the top of the bottle rests a water-jacketed, lead condenser, extending through the roof of the house. An air jet placed in the upper end of the stack contributes the means of drawing the vapors from the nitrator.

A. Losses of Nitrobenzene in Waste Acid

When the nitrobenzene in the waste acid is not extracted by counter-current washing with benzene next to be nitrated, it is recovered from the spent acid by allowing the acid to settle in large lead tubs from eight to twenty-four hours, the length of time for settling depending on production demands. The percentage of nitrobenzene soluble in waste acid depends upon the temperature. In hot summer months it has been found as high as 1 percent while in winter when the nitrobenzene freezes, the percentage drops as low as 0.45 percent. The average amounts of nitrobenzene which were determined by making ether extracts on the waste acid, for the latter part of August and September, proved to be 0.7 percent which is about 0.8 percent loss of the percentage yield.

In separating the acid oil from the spent acid a considerable loss is entailed which cannot be readily estimated. The waste acid is drawn from the tubs first, the nitrobenzene is then drawn down into a lead baffle box, and from there the upper layer of the oil is run from cocks placed at different levels. The losses are due to incomplete separation of the nitrobenzene from the waste acid.

The losses in the foregoing respects could be eliminated however by

I. The use of slope-bottomed separators provided with outlets for drawing off " straight " waste acid at the base, and side outlet for running off the nitrobenzene.

II. Use of the upper layer in the spent acid tanks, along

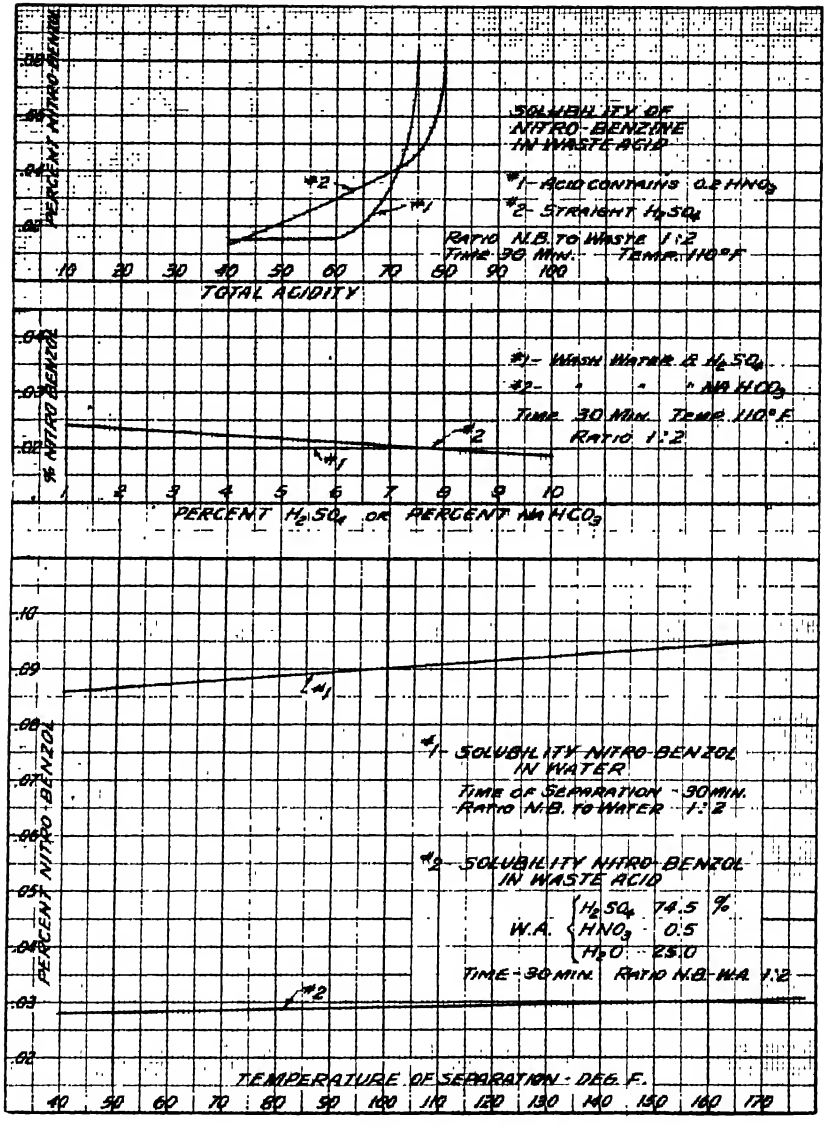


FIG. 17.
Nitrobenzene Solubility Curves.
1, in waste acid; 2, in wash waters; 3, in water.

with NB saturated waste acid remaining in the separating tanks, as cycle acid for following nitrator charges.

B. Percentage Loss of Nitrobenzene in Wash Waters

The nitrobenzene after separation from the waste acid in the settling tubs is run into a horizontal tank, supplied with a draw-off line at the base for the removal of any waste acid that again settles out, the waste acid being drawn off into a bucket. From this blowcase the nitrobenzene is delivered to a neutralizing tub. This is equipped with air steam and an agitator. In washing each charge, three washes may be given, the second of which contains sodium bicarbonate for the neutralization of any acid. The washes are made at a temperature of about 110° F. and are agitated with steam and air for about one-half hour, after which they settle for an equal time. The wash waters are drawn off at different levels, and are allowed to run into a series of three wood catch boxes, the last of which empties into a ditch.

The average amounts of nitrobenzene, determined by making a great many ether extracts on samples taken from the boxes at different times, were as follows:

Catch Box No. 1	*Catch Box No. 2*	*Catch Box No. 3*
% N.B. 0.108%	0.0736%	0.066%

The amount of nitrobenzene per charge passing into the ditch represents a loss of 0.16 percent of the percentage yield.

II

Experimental Nitrations Using Undersurface Feed

In order to introduce the acid beneath the surface of the benzene in the nitrator, a lead pipe is attached by bands to one of the agitator shafts and made to extend the full length of one of the submerged propeller blades. The end of the pipe makes a bend and comes up. The upper end of the pipe is burned to a funnel, encircling the shafting, the inside lip of which attains the height of the outside. The mixed acid line leading to the nitrator terminates directly above the funnel. This ar-

rangement eliminates practically all of the benzene and nitric losses up the fume stack so that a condenser for the Woulf bottle is no longer required.

It was found that when water is used as a refrigerant the reaction runs smoother and is considered safer because temperature fluctuations are immediately recorded, and the operator can gauge maximum rises and falls whereas when brine is used such peaks or drops do not record as quickly.

The results on a number of experimental runs using this undersurface feed were as follows:

	Nitration			
	1	2	3	4
Lbs. Benzene	2,400	2,400	2,401	2,402
Lbs. Mixed Acid	4,900	4,958	4,939	4,939
Actual HNO_3 Ratio	.807	.818	.815	.815
Temperature Condition of Nitration	70° F. 140° F.	70° F. 140° F.	70° F. 80° F.	55° F 60° F.
Time of Nitration (hours)	3 hrs.	3½ hrs.	3½	5½
Time of Cooking Charge	1 hr	1 hr	3 hrs	3 hrs.
Lbs. Acid Nitrobenzene	3,668	3,680	3,683	3,676
Percent Acid in NB calculated as Waste Acid	0.21%	0.23%	0.22%	0.22%
Lbs. calculated NB (lbs.)	3,660 lbs.	3,671 lbs	3,675	3,668
Yield on Benzene, %	152.5%	152.9%	153.0%	152.7%
Time of settling charge	17 hrs	17 hrs.	16 hrs.	15 hrs
% NB in Waste Acid	0.55%	0.61%	0.58%	0.71%
Temperature of NB when separated	63° F	67° F.	64° F	67.0° F
Analysis of % HNO_3	0.23%	0.56%	0.35%	0.33%
Waste Acid % H_2SO_4	70.95%	72.45%	71.6%	71.7%

The following general conclusions made by the study of plant conditions may be summarized as follows:

1st. That it is manifestly impossible to obtain nearly theoretical yields by nitrating with the theoretical acid ratio, owing to unavoidable losses during nitration.

2d. That practically no HNO_3 is lost during the cooking period if the temperature is raised from 70° F. to 140° F. with the last 1,000 lbs. mixed acid instead of 1,500 lbs.

3d. That the undersurface feed entirely eliminates any visible trace of benzene fumes.

4th. That it is unnecessary to nitrate at lower temperatures

in order to avoid loss of benzene, as shown by runs Nos. 2, 3, 4 in the above chart.

5th. That it is desirable to use enough HNO_3 to leave about 0.75 percent in the waste acid. Analysis of waste acid shows it to be possible to strip the mixed acid of HNO_3. A 0.75 percent excess allows for any loss in fumes and for the 0.3 percent to 0.5 percent remaining in the spent acid, while the excess over the theoretical amount required is not sufficient to cause dinitration in the relatively short time and at the low temperatures used in nitration.

6th. That as long a time as possible for settling the charge after nitration is required to reduce the acidity of the nitrobenzene.

7th. That cooling the waste acid while settling is desirable to decrease the solubility of the nitrobenzene.

8th. That countercurrent washing of outgoing waste acid with benzene to be nitrated practically eliminates losses due to solution in waste acid.

NITRATION OF BENZENE

Efficiency of Nitration Using Sleeve and Propeller Agitation

Introduction

It has been generally believed that the cooling coils in the paddle-type nitrator were not very efficient. This was obvious when it was shown during test runs that a heat transfer of only 70–80 B.T.U. was obtained, and this fact explained the comparatively excessive time, six to eight hours, to complete a nitration of 2,400 lbs. benzene in this style of nitrator using surface feed.

From investigations made with a Hough Nitrator, along with a general study of heat transfer and types of agitation, the following conclusions are summarized:

It has been shown during the course of investigation that by the use of a Hough Nitrator, or the installation of the propeller and sleeve agitation in the coil type of nitrator, a much better heat transfer may be obtained with shorter time of nitration.

Experimental Nitrations

In order to ascertain correct values for the thermal efficiency of this latter type of apparatus a nitrator having a capacity of approximately 325 gallons of liquid was set up for experimental work. This was equipped with propeller and sleeve agitation, and the coils were distributed as in the Hough Nitroglycerine Nitrator in staggered concentric layers, in place of the usual bank around the inside shell of the nitrator. With these changes it was found that the heat transfer increased from 60 to approximately 200 B.T.U.

Various types of propellers were installed and definite data obtained on each. The most satisfactory results were obtained when using a three-blade propeller, 24 inches in diameter with a 24° pitch. With this agitator, together with 103 sq. ft. of cooling surface properly distributed, it was found possible to nitrate 750 lbs. of benzene in 110 minutes with a heat transfer of 200 B.T.U. per hr. per sq. ft. per degree difference in temp., using water as a refrigerant at an ingoing temperature of 78° F., supplied at the rate of 140 gallons per minute.

Plant Nitrations

The following data, supplied by one of the most successful manufacturers of aniline oil, shows plant operating results, using a modified Stevens Nitrator with (draft tubes) sleeve and propeller agitation for the nitration of benzene.

Nitration with Sleeve and Propeller Agitation

Charge of Benzene	6,000 lbs
Time of Nitration	2½ hrs.
Teperature of Nitration	50–60° C.
Time of Digestion or Cooking at 50–60° C.	2 hrs.
Yield per 100 lbs. Benzene	154–155 lbs.
HNO_3 in Waste Acid	0.3 percent

The above results are obtained in a closed system of nitration, using a cycle acid heel and top feed.

Discussion of Propellers

The most characteristic points of propellers when functioning in a sleeve are briefly as follows:

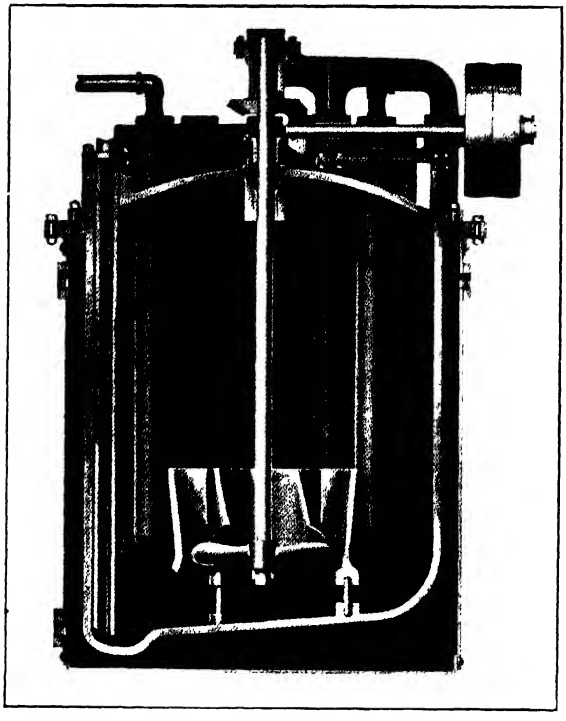


FIG. 18.
Nitrator (with draft tube circulation).
In newer design the finger cooling tubes are replaced with a solid bank of coils.

1. Each propeller must attain a certain speed or number of r.p.m. before it shows an appreciable pumping capacity. This is due to slippage.

2. The greater the pitch, the less the speed; or the greater the speed, the less the pitch of the propeller to pump the same volume of liquid. In other words, a propeller of high pitch can run at a lower r.p.m. and can start its pumping action before a propeller of shallow pitch running at higher r.p.m.

3. The size or diameter of a propeller is a greater factor in determining its pumping capacity than its angle of pitch.

4. The amount of slippage encountered is great, due to the swirl caused by the propeller functioning in a sleeve. The greater the pitch the greater will be the swirl. This may be

overcome to a large extent by fluting the sleeve or by placing stationary propellers of opposite pitch within the sleeve at a short distance above the revolving propeller.

5. In order to prevent any breaking of the surface where the liquid is forced upwards from the sleeve, a baffle must be installed directly above the sleeve. This should deflect the liquid out and down into the body of the charge. Thus, when the liquid passes through a large number of perpendicular cooling tubes, a maximum cooling effect is obtained, and simultaneously prevents considerable loss of hydrocarbon and nitric acid by eliminating the surface break. If the baffle is adjustable so that it can be raised as the charge is built up, and can always be maintained about 2 inches below the surface of the hydrocarbon, the best results will be obtained.

General Remarks

In order to obtain the maximum efficiency with this type of nitrator, it has been demonstrated by a number of tests that high velocity of the liquid in the sleeve and past the coils, together with cooling water of sufficient quantity and low temperature are essential.

To obtain the desired velocity of the liquid through the sleeve and past the coils is a matter of speed or r.p.m. of the propeller used, which determines the pumping capacity and, consequently, the number of times the charge is turned over per minute.

The ratio of the size of propeller best adapted to this type of nitrator is approximately 1 : 3 compared with the diameter of the nitrator. In this proportion the r.p.m. of the propeller may be kept fairly low and still obtain the desired velocity without causing emulsification of the two layers in the nitrator.

The sleeve, which is slightly larger in diameter than the propeller used, is made of cast iron, or preferably may consist of lead or iron cooling coils placed in the center of the nitrator and supported by legs at the desired height, to allow sufficient space for the liquid to be returned to the sleeve after it has been forced out of the top and down past the coils. The height of

the sleeve must be such that it comes within two or three inches of the top layer of cooling coils, which usually occupy about one-half the depth of the nitrator.

Two stationary propellers of opposite pitch are placed inside the sleeve, a few inches above the revolving propeller, in order to cut down the swirl, thus increasing the pumping capacity of the propeller. As the propeller revolves the liquid inside the sleeve is forced up through it and strikes an annular baffle plate, elevated above the top of the sleeve, thus diverting the flow of the liquid in a lateral, and thence vertical, direction past the cooling coils.

The distance of the baffle above the top of the sleeve must be such as to cause no appreciable resistance to the liquid, or nitration will take place inside the sleeve.

The nitrating acid is fed into the spent or cycle acid by means of an annular acid distributor, placed a few inches directly under the revolving propeller. By feeding the mixed acid into the cycle acid the nitration is made with a fortified spent acid which gives a perfect temperature control.

In this type of nitrator two distinct layers of liquid are maintained throughout most of the nitration, a lower one of waste acid, and another one of benzene and nitrobenzene which lies on top. As the propeller forces the cycle acid which has been fortified by the addition of mixed nitrating acid through the ports of the sleeve, it attacks a portion of the benzene layer without breaking the surface. As the nitration nears completion the specific gravity of the cycle acid decreases and the nitrated benzene increases to approximately the same gravity, after which the two liquids are uniformly mixed by the agitation, but separate very rapidly when the agitation is discontinued.

A syphon or overflow system is used to maintain constant level in the nitrator. The overflow is so constructed that it carries off the cycle acid from the bottom of the nitrator as near the center as is practicable.

The amount of hydrocarbon carried off through the overflow system is governed by the following:

1. Speed of agitation.
2. Height of the propeller from the bottom of the nitrator.
3. The shape of the bottom of the nitrator.

The most satisfactory results may be obtained by running the propeller at a speed which insures turning the charge over from two to three times per minute, and placing the propeller at such a distance above the bottom of the nitrator that very little agitation occurs at the bottom layer of the cycle acid. A cone-shaped-bottom nitrator doubtless is more practical as the syphon or overflow system could be placed directly in the center of the nitrator where there would consequently be more or less of a dead pocket of cycle acid, thus eliminating a large amount of the hydrocarbon being carried off with the cycle acid.

SYSTEM OF NITRATION BY CYCLE ACID IN THE HOUGH NITRATOR *

Foreword

The Hough Nitrator designed for benzene nitration is built with two tunnels, one on either side of the body of the nitrator. There are two impellers revolving at from 200 to 400 R.P.M. according to the size of the machine. In this type, the contents of the nitrator are completely circulated once in one minute, or in other words, the rate of circulation of the liquid through the tunnels will, in the large size machine, be about 2,500 gallons per minute.

Well down the tunnels, and under the impellers, is the injector for the hydrocarbon to be nitrated, and for the nitration acid. The latter is forced in a small stream into the benzene-cycle acid mixture so that approximately one pound of incoming nitrating acid comes in contact with 1,000 pounds of material in the nitrator. This is an ideal condition to obtain in nitration, and prevents any local rise of temperature.

From a glance at the drawing of this machine it will be seen that the circulation of the liquid is from the lower part of the

* Contributed by A. Hough.

tunnel over the port and into the body of the machine. It will be readily seen then that in order to function properly, the ports must be covered at the start with a liquid heavier than the hydrocarbon to be introduced.

The Cycle Acid System of nitration brings this condition about in an ideal manner.

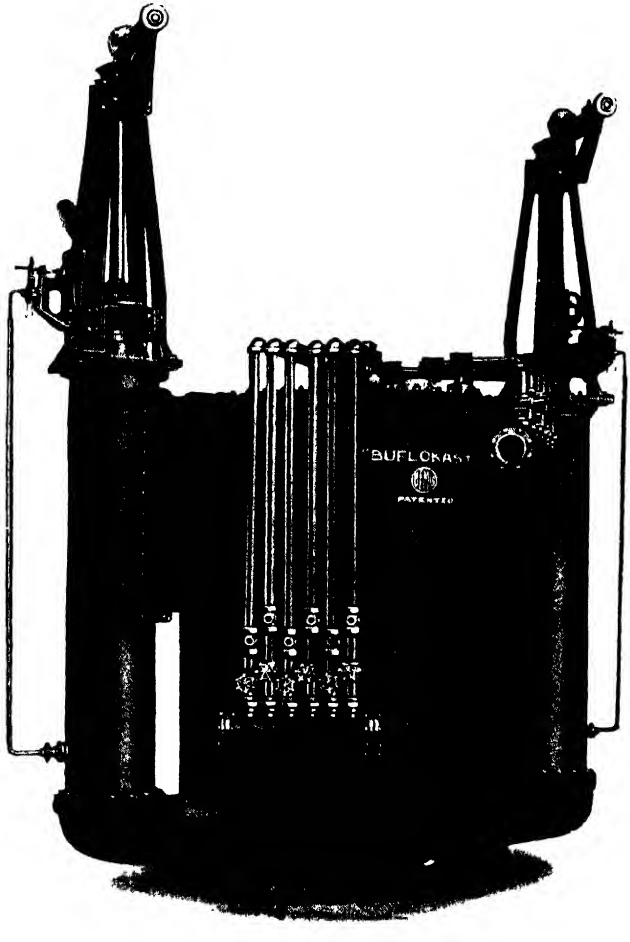


FIG. 19.
Hough Nitrator.

Procedure

Nitration of Benzene—Hough Nitrator.

The method of nitrating with cycle acid is the general principle, the underlying principle is that considerable weight of material, inert as far as conditions of nitration are concerned, is introduced into the nitrator. Both the sulphuric and nitric acids employed for nitration are of minimum specific heat, whereas the cycle acid is of maximum specific heat. It follows therefore that during the process of nitration, the heat developed is quickly absorbed in the cycle acid and conducted away by means of the cooling coils, and to a smaller extent by radiation through the shell of the nitrator.

For the first run of the nitrator a charge of sulphuric and nitric acid, corresponding to the normal spent acid obtained from the nitration we have in mind making, must be prepared. This acid is placed in the nitrator so as to cover and just overflow the ports of the machine. The agitator (impeller) is now started up, and the whole of the benzene charge is run into the machine through the injector pipes at the side of the tunnels. It is quite immaterial how fast this benzene is run in, as the agitation is so perfect, and the amount of nitric acid in the cycle acid so small, that practically no elevation of temperature occurs. All the benzene being in, the nitrating mixed acids are forced in through the injector pipes just as fast as possible, keeping the temperature within the desired limit. It is quite possible to conduct a run in this way at a temperature of 100° C., without the least danger of the temperature rising beyond control. In fact in these machines, with the extent of cooling surface provided, it is impossible for the reaction to elevate the temperature above that desired. It will be readily seen that at this temperature nitration is conducted very rapidly, and not more than one-half the time is required to complete the reaction as would be necessary by the old method where 60° C. is the limit of temperature during the addition of the benzene. After all the nitrating

acid has been added, the temperature may be held at 90° C. for two hours and the reaction is complete.

Reverting to the addition of the nitrating acids. At the moment these acids are being added, the withdrawal of the original acid is started (cycle acid), just as much cycle acid is drawn from the nitrator in volume as there is nitrating acids added. Or in other words, the volume in the nitrator is maintained at a constant. The withdrawal of the cycle acid is done from a cock placed at the lowest point of the nitrator, and where there is least agitation. A small amount of nitrobenzene of course is carried along with the cycle acid, but this is not lost as it is returned on the run of the next charge.

The withdrawal of the cycle acid is termed "bleeding" the nitrator, and this acid resulting from the "bleeding" process is of course returned to the nitrator, the benzene added, and then nitrated as usual.

An improvement recently developed by Dr. Hough for his nitrator is an extension in the form of a long tube or well, attached to the bottom of the machine. The "bleeding" cock is attached to the end of this tube, and the cycle acid may be drawn therefrom with practically no nitrobenzene in it.

The advantages of the cycle acid system may be summed up as follows:

1. Much greater capacity in output per cubic foot of nitrator space.
2. Absolutely no danger of firing a charge of benzene.
3. Less benzene volatilized, and therefore less to take care of with condensers.
4. The possibility of being able to use a much stronger mixture of nitrating acids than is usual with the older process.

Separation of the nitrobenzene from the spent acids is of course done in a separate vessel, the nitrator being held exclusively for nitration purposes.

It will be seen that during the first few runs, the spent acid will vary slightly, rising in strength. But after a few runs this will become a constant.

The composition of the nitrating acids permissible with the cycle system is as follows:

HNO_3 .....34%
H_2SO_4 .....57% DVS 3.0
H_2O 9%

This composition may be varied considerably to suit the conditions at the factory, due consideration being given to the quantity of sulphuric acid required for dehydration purposes.

Representative Charge for Nitrator Operating on the Cycle System

The following data is taken from an actual nitration using a very large machine. Owing to the difficulty of castings, smaller sizes are at present being recommended. The data below however is correct for all sizes of machines.

Initial charge of weak acid to represent cycle acid . . 9,000 lbs.

Composition of above: H_2SO_4, 83%
HNO_3, 2.3%
H_2O, 14.7%

Nitric content includes low oxides of nitrogen.

Charge of benzene ..... 10,000 "
Charge of mixed acid . . . . . 23,300 "
Composition of mixed acid (99% Acidity):

H_2SO_4, 62.8%
HNO_3, 36.1%
H_2O, 1.1 } .. . . . . 5.5 DVS

Nitric content includes low oxides of nitrogen amounting to about .2 percent.
Yield of nitrobenzene about 15,698 pounds.*

Length of time required to introduce benzene into inert (cycle) acid, about one half hour.
Time required to inject nitrating acid, one hour.
Time required to cook at 90° C., two hours five minutes.
Total time for run, 3 hours 35 minutes.

* The above yields are based on 100% C_6H_6 as used. No allowance is made for losses in handling. The nitrobenzene dissolved in the waste acid is recovered by counter current washing, with the benzene next to be nitrated.

CHAPTER VIII

COST FACTORS IN PRODUCTION

Production without profit attracts neither men nor money. Profit is normally dependent on costs more than on selling price. For a brief span of years (during the World War), however, the American chemical industry enjoyed the sensation of producing in a seller's market. Price to those requiring materials was secondary to obtaining delivery of products urgently needed. Thus, with a large margin of profit beckoning the producing chemical organizations, a hasty and riotous development was indulged in. Many novices joined the ranks of the more established producers and for a while they were all well rewarded. Soon, however, the day of reckoning came and many producers fell by the wayside, for the justification of inefficient operation had ceased to exist and only those who applied the science of chemical control could hope to be rewarded.

A glance at the chart showing the cost of chemicals since 1914 reveals the enormous inflation of prices during the duration and for a brief period after the war. During this time the American dye industry came into existence. True, there were several small enterprises doing meritorious work who managed to eke out an existence against the sharp business practices used by foreign organizations, but their existence meant very little to the American people. This span of years, 1914 to 1922, may be roughly divided into four periods:

1914–1916, Experimentation
1916–1920, Expansion
1920–1921, Deflation
1922– , Consolidation

Very little further need be said regarding the above chart to those who have gone through these periods and have witnessed the changes which economic conditions made necessary.

At the outbreak of the war there came to the dyestuffs con-

sumers a panicky realization that foreign dyestuffs might not get through the barrier of blockades. The infant industry here was beseeched to extend itself to supply a portion of the immediate requirements. A period of hasty experimentation set in. Dyestuffs, poor and otherwise, found eager purchasers. The industry then began to develop to gigantic proportions. Costs—yields—economies were ruthlessly disregarded until the retrenchment move at the close of the war, already in operating evidence in other industries, bumped heavily into the chemical consuming market. Then came a period of idleness and reflection, followed by an appalling deflation of every phase of the industry.

A realization had come about that hereafter products had to be produced economically. These products had also not only to compare favorably with foreign materials but had in many cases to be far superior in order to overcome inherited prejudice and alien propaganda.

Factors Affecting Costs

Successful manufacturers need no reminder that present competition demands highest efficiencies in every phase of operation. An attempt will be made, however, to set down several broad divisions, for the benefit of the student, wherein, if the highest efficiencies are reached, sound economical operation must follow:

I. Determination of best method of production.
II. Selection of best type of equipment.
III. High operating efficiencies.
IV. Large productivity for equipment used.
V. Purchase of materials at favorable prices.
VI. Low overhead and fixed charges.

The numerical arrangement of the above cost factors represents their relative importance.

Discussion

I. It is unquestionably true that the choice of maintenance of the most efficient method of operation is of the utmost im-

portance. The largest organization possessing every facility for economical operation, and in a position to install the most expensive machinery, cannot compete favorably unless the system adopted contains certain inherent characteristics making for low cost production. A review of the chapter on " Various Methods of Manufacture " reveals the enormous gaps which exist between the several processes. The chapter on nitrobenzene manufacture indicates that a great disparagement also exists between nitration with surface feed and with undersurface feed. Also a similar advantage or handicap exists in using the sleeve and propeller nitration with constant level charge as compared to paddle agitation with constantly increasing charge. The above references should indicate quite clearly that the foremost item in the economical production of aniline oil is the selection of the right process. The subject justifies continual investigation, particularly along new lines, for with the march of progress in the manufacture of equipment, processes once impossible are now feasible.

II. The selection of equipment is one which is receiving considerable attention in America at present. This, in a large measure, is due to the beneficial influence of the chemical expositions, at which the manufacturers of chemical equipment have taken the opportunity for aggressive sales campaigning. As pointed out previously, large size equipment within reasonable power loads is conducive to increased production at lower operating costs. Smaller vessels multiply the sources of loss and require more operating labor. For equal capacity, large-sized units require less capital outlay, less floor space and less supervision.

III. Probably the most interesting document to the operating chemist is the periodical operating report. This report shows the yield of finished product from raw material used, based on actual physical inventories. The magnetism of these reports giving information as to the successful conversion of raw ingredients into salable finished products is the attraction that keeps many men in a field, which is often deleterious to health, and comparatively unremunerative as to value received for services rendered.

No mention is made in the list of factors affecting costs as to the operating labor burden. In fact this is unnecessary. A handful of men can operate an aniline plant producing a million pounds of finished product monthly. The value of the raw materials used is enormous, probably about ninety thousand dollars, yet the entire operating labor cost would not exceed five thousand dollars. It is quite evident that any increase of two percent in yield of finished product from raw material used would be equivalent to thirty percent of the labor costs.

IV. Continuous operation at maximum capacity makes for lower costs and smoother operation. This is so universally recognized as to warrant no further comment.

V. Firmly established companies, with extensive credits, are unquestionably in a position to obtain better contracts for raw materials. The greater the volume of business, the greater will be the concessions for their trade. Of course an alliance of organizations whereby " favored nation " clauses are incorporated so that one concern can obtain benzene at a very low price, while the rest of the market is begging for that material at competitive prices, makes for an inequitable but actual basis of competition.

VI. A number of comparatively small plants are producing aniline today despite several serious handicaps. They do not consume a large percentage of their product, nor do they obtain the best costs on raw material. In order to offset these handicaps, the benefits of a more personal supervision in a smaller plant enter. The large organization, with a considerable overhead burden and oftentimes subjected to financial manipulation, taps the business for what may amount to a disastrous drain, whereas the smaller producer limits this cost item to the lowest possible figure.

Each system of operation requires a different set of cost figures for operating expense—power—and fixed charges. Even the same unit will require modifications each month based on production and other factors. It is thus only possible to indicate in a general but quite accurate way the factors in determining the cost of producing aniline.

STAGE I

Nitration of Benzene to Nitrobenzene

Molecular weight benzene, C_6H_6	78
Molecular weight nitrobenzene, $C_6H_5NO_2$	123
Theoretical yield	157.7
Standard yield for determining costs	153.5

To Produce 100 lbs. Nitrobenzene

*65.15 lbs. Benzene, @ 3.0 cents	$1.95
71.00 lbs. H_2SO_4, @ .75	.54
55.00 lbs. HNO_3, @ 6.00	3.30
1.00 lb. Na_2CO_3, @ 2.00	.02
Total Material Cost	$5.81

Credits

69.0 lbs. H_2SO_4 in waste acid, @ 0.5 cents	.345
.9 lb. HNO_3 in waste acid, @ 5.0 cents	.045
	.390

Therefore, Net Material Cost per 100 lbs. N.B. $5.42

Operating Costs	Operating labor and Direct supervision Repairs Labor Repairs Material Supplies	.15
Power Costs	Electric Steam Air Water Brine	.20
Overhead	Administration Depreciation Insurance Fixed charges	.52

Net cost per 100 lbs. Nitrobenzene $6.29

* Benzene at 22 cents per gal.; add 1/8 cent per pound to final cost for every cent increase above 22 cents per gallon as cost of benzene.

Nitrobenzene—Percentage Cost Analysis *

Operating Cost	$\frac{.15}{6.29}$	= 2.4 percent of total cost.
Power Cost	$\frac{.20}{6.29}$	= 3.2 percent of total cost.
Overhead	$\frac{.52}{6.29}$	= 8.3 percent of total cost.
Raw Materials	$\frac{5.42}{6.29}$	= 86.1 percent of total cost.

STAGE II

Reduction of Nitrobenzene to Aniline

Molecular weight benzene, C_6H_6	78
Molecular weight nitrobenzene, $C_6H_5NO_2$	123
Molecular weight aniline, $C_6H_5NH_2$	93
Theoretical yield benzene to aniline	119.2
Standard yield benzene to aniline	109.75
Theoretical yield nitrobenzene to aniline	75.6
Standard yield nitrobenzene to aniline	71.5

To produce 100 lbs. Aniline from Nitrobenzene

140 lbs. Nitrobenzene, @ 6.29 cents	$8.80
160 lbs. Iron borings, @ .75 cents	1.20
15 lbs. HCl or equivalent $FeCl_2$, @ 1.00 cents	.15
Total Material Costs	$10.15
Operating Costs: Labor operating, Repairs, Supplies, Direct Supervision	$1.00
Power Costs: Electricity, Steam, Air, Water	.80
Overhead: Administration, Depreciation, Insurance, Fixed charges	.50
Total Material Costs per 100 lbs. Aniline	$10.15
Total Net Cost per 100 lbs. Aniline	$12.45

* Numerator = cost of each phase of production.
Denominator = total net cost.

To the experienced operator it is very apparent that the above figures call for excellent operating control, and the introduction of raw materials at very favorable prices. The cost figures also presuppose some regularity of operation as they do not provide for long periods of non-production. However it must be remembered that these figures are set forth merely to convey the importance of obtaining factors. When these are known they make for more efficient operation due to the fact that each charge can be scrutinized.

Aniline—Percentage Cost Analysis *

Operating Costs	$\frac{1.00}{12.45}$	=	8.0 percent of total cost.
Power Costs	$\frac{.80}{12.45}$	=	6.4 percent of total cost.
Overhead	$\frac{50}{12.45}$	=	4.0 percent of total cost.
Raw Materials	$\frac{10.15}{12.45}$	=	81.6 percent of total cost.

THE CHEMIST'S BUDGET

Business may be broadly divided into three elements, namely: production, marketing and administration. At the helm of every organization, coordinating these functions, and guiding its destinies, presides the manager. In order to insure profitable operation he must know, as part of his knowledge of the company finance, just what the monetary demands of each of the above divisions should and can be. Based upon this knowledge, and in order to minimize occurrences tending to cause a severe drain on the company resources, a graphic detailed chart embodying the financial policy of the executive is prepared. This document is the *Budget*. In it the estimated income is pro-rated among the three elements, due provision being made for profits, expansion and emergencies. Each is allotted a calculated per-

* Numerator = cost of each phase of production.
Denominator = total net cost.

centage of the available funds, based on the results of experience and policy, so that it may carry on its work to the best interests of the entire organization. Each element of the industry in its turn prepares its departmental or divisional budget in order that the operation of the separate units of each division may all cooperate to the proper fulfillment of basic plans. Adaptation to such budgets by every department are the semaphores of business progress. As soon as prescribed limits are run by, then danger looms up and the best laid plans may come to naught. Although few industrial chemists are called upon to prepare such financial budgets, practically all of them are confronted with the ramifications of this industrial guide and it behooves every chemist, whether engaged in control, research, operation, or management, to ascertain just how far he can legitimately proceed in the expenditure of funds.

The operating chemist is chiefly concerned in a complete budget of his own. In this budget there is no direct expenditure of money. The expenses here are material ones, all charged against *waste*. As no business can be run without cost, so also, no chemical operation can be run without loss and the expense budget concerns the business manager, as does the "*Sources of Loss Chart*" the chemical engineer. In this chart the chemist needs to know just what legitimate material expenses his operation may suffer. The legitimate losses are based on the best possible functioning of each phase of the total operation. Opposite each of these items is placed the calculated or estimated percentage of material expenses. The total is then charted and a standard yield adopted. From such considerations the chemical budget is prepared. With such a guide, light can be thrown on the discrepancies that exist between theoretical yields and actual accomplishments. An insight may now be gained as to what happens to the thousands of pounds of raw materials going into the cycle here and being dissipated somewhere before the finished product is ready for shipment.

Nothing is quite so important in the control of a given system of production as the definite knowledge of losses at each point.

It is true that sometimes shrinkage has to be estimated, but such instances make up but a small fraction of the total yield loss.

In order to obtain data as to the legitimate losses in each phase of operation and later for use in checking up operating procedure, every avenue of material escape should be examined to determine its place in the "*Sources of Loss Chart.*" From the results obtained by laboratory control, ways and means can be devised and adopted either for maintaining or improving standardized conditions. It is said that eternal vigilance is the price of good yields and it is indeed very true that exacting supervision over minute details leads to the limitation of operating losses well within the permissible limit. The limitation of material expenses by budget is thus seen to be a faithful guide in the adoption of methods to eliminate useless waste in the handling of materials. The chemist in his profession has been the most important factor in the war on waste, and his great accomplishments have already been heralded far and wide. Many industries once unprofitable are now financially stable. Many obnoxious bi-products are now bringing revenue into the coffers of industry. Every chemist cannot gain honors in achieving new discoveries but each one concerned with productive operations can set for himself a high mark to shoot at, so that in the interest of material conservation unnecessary waste may be eventually eliminated. The reader must realize that the constant migration of workmen from place to place soon makes for similarity of operating technique.

Dr. Edward Fierz David in his work on "Dye Chemistry" notes that "the development of the dye industry has brought it about that many once carefully guarded secrets are now matters of general knowledge." Ullman's great "Enzyklopaedie der Technischen Chemie" has shown that many processes have long been known to most manufacturers. Again, the migration of various workmen has made it inevitable that every important improvement becomes known to competitors in a relatively short time. The success of the great dye factories,

therefore, is not founded on any secret processes, but upon traditions of many years, upon excellent organization, and on the specialties which are protected by patents."

Likewise the constant advertising on the part of equipment manufacturers will lead ultimately to the economical scrapping of antiquated equipment to make room for machinery of more efficient design. As stated previously, the adoption of the best process which is worked in the most approved type of apparatus is the most important factor in chemical production. It is a notable fact, however, that many operations employing identical equipment and similar procedure will work successfully in one factory and fail in another. To account for such a discrepancy one factor is outstanding, the factor of supervision. In one case every detail is checked up, every loss is accounted for—waste is eliminated; in the other, material is put into the system and the only check on operations is the rude awakening caused by poor yields obtained at the end of the process.

The material budget constitutes the first or prime cost. It is by far the most important element in chemical manufacture (see aniline costs). Roughly speaking, the prime cost for most intermediates is ordinarily twice as great as all the other contributing factors entering the cost sheet. An inspection of the Aniline Cost Outline will quickly reveal the importance of this item in its manufacture.

It is not the province of this book as a chemical treatise to dwell at length on the other items entering into the cost of production. Such a dissertation belongs logically to the publications on Industrial Management. A few leading remarks will, therefore, only be made in the elaboration of each item.

Operating Labor and Direct Supervision

Under this head is included the wages of operators, foremen, and supervisors carrying on the work of production. Technical supervision should show a profit and ought not be a burden to the operation involved. Either through increased yields, greater productivity, or institution of other economies,

the chemical engineer should prove that his presence is an asset, and not a liability. In the case of well-established operations where numerous chemists, or chemical advisory boards, have already brought a process to a high degree of excellence, the engineer should show marked executive ability in handling men, conducting and coordinating operations, and maintaining therein the highest established standards. The recruiting and maintenance of an operating crew of high intelligence is a distinct and valuable asset. As operating labor is seldom a very crucial item of expense it can be truly said that men of the better grades pay for their increased earnings by producing more efficiently than labor with a lower level of skill.

Repairs—Labor. Repairs—Material

There is more room for fluctuation here than with the control of operating labor expense. This is due, both to the destructive nature of chemical reactions and to the uncertainty connected with human control. The erosive, corrosive, dissolving, disintegrating actions to which practically all chemical apparatus is subjected naturally make for a comparatively high maintenance factor. Incompetence or negligence on the part of the operator oftentimes contributes towards swelling the normal repairs charge.

Two factors may be employed in controlling and curtailing what may be considered legitimate charges. First, the employment of departmental repair men, who specialize in maintenance for certain processes and become expert at such work. This arrangement leads to a very close cooperation between operators and repairmen. No time is lost in the preparation of materials nor unnecessary holding up of repairs. Secondly, a study of the chief items going into the repair bill should be made to determine whether certain items can be eliminated by a change in the method of handling materials or changing the operating technique. Oftentimes this study leads to the substitution of repairs material yielding more economical service.

Supplies

This item is largely a housekeeping expense and as a rule not subject to great fluctuations. As in our homes, however, it may become pervious to a system of laxity and extravagance if not closely watched.

Power Costs

Under the term Power Costs is included steam, electricity, water, compressed air, brine and, in some instances, service of a central vacuum pump. The aggregate of all these items is considerable and should be the subject of close cooperation between the power engineer and the operating chemist. Despite the fact that power costs are normally higher than supplies and repairs material, very little accounting or metering of the former is undertaken while elaborate systems of inventories and bookkeeping are used in the handling of the latter. One would hardly think of guessing at the cost of supplies going to an operation, yet very little is thought of estimating water, steam or electric consumption in individual processes. Power is a definite and rather costly commodity, and as such should be carefully metered not so much for the sake of accurate costing, as for the possibility of effecting considerable economies by a careful study of a daily itemized power bill.

Generally speaking it suffices to say, wherever possible, use the cheapest form of power. Arrange equipment to utilize advantages of gravity flow. Utilize exhaust steam. Resort to river-water or deep-well-water instead of a costly municipal water supply. It is undoubtedly true that many an operating chemist who guards his raw materials well will often be lax in controlling power items entering into his operations.

Budget

Conversion Benzene to Nitrobenzene

Theoretical yield 157.7
Standard yield .....153.5 } per 100 lbs. of benzene used

Material Nitrobenzene

Sources of Loss	Calculated Loss	Actual Loss	Loss Previous Periods
Impurities in benzene	0.8		
Loss in handling based on discrepancies or shortages	0.2		
Losses in nitration	0.9		
Losses waste acid separation	1.0		
Losses neutralizing washes	1.0		
Operating allowance	0.3		
	4.2		

Note: Several plants claim standard operating yields better than 153.5; their efficiency in reduction is however not quite as high as noted in the following table. This may be due either to the H_2O content, or inert material content of the nitrobenzene delivered to the reducer houses, and for which credit is claimed during the nitration stage. Where the waste acid from benzene nitration is washed by the benzene next to be nitrated the loss for this phase is lower.

Budget

Conversion Nitrobenzene to Aniline

Theoretical yield 75.6
Standard yield .....71.5 } per 100 lbs. nitrobenzene used.

Material Aniline

Sources of Loss	Calculated Loss	Actual Loss	Loss Previous Periods
Impurities in nitrobenzene	0.5		
Loss in reduction through vent and in operation	0.5		
Losses in sludge waters	1.2		
Loss in separation of oil (aniline water, press cake, etc.)	0.9		
Losses in rectification	0.5		
Operating allowance losses dependent on simplicity of system	0.5		
Standard loss	4.1		

CHAPTER IX

THERMAL FACTORS, REDUCTION OF NITROBENZENE TO ANILINE OIL

Heat studies made on the reduction of 1,200 lb. charges of nitrobenzene reveal that the reaction is quite exothermic and that the liberation of heat continues after all the iron has been fed into the reducer. The figures below show "the B.T.U." generated by the reaction and the B.T.U. delivered by pressure steam during the Feed and Reduction of a 1,200 lb. charge.

	B T U Generated	B T U. Delivered by Press Steam
Feed	1,805,000	0
Reduction	488,000	1,343,000
Distillation		5,585,000
Totals	2,293,000	6,928,000
Heat of conversion per pound nitrobenzene	1,911	5,773

The aniline oil in the reducer charge was steam distilled into a receiver and later delivered to the purification house. At a glance one can see the enormous amount of steam consumed during the distillation.

Aniline Reducer Test

Equipment

The equipment upon which the test was run consists of one reducer and its accessories, all of which are standard. The accessories are:

1 Condenser (submerged coil type)
1 Nitrobenzene Weigh Tank
1 Aniline Water Tank
1 Scale and necessary boxes for weighing iron borings
1 Distillate Tank
1 Dephlegmator

The reducer is equipped with a motor-driven agitator and also with steam connections which introduce steam directly into the reducer. The piping is such that the vapors condensed in the condensers may be returned to the reducer or may be directed to

the distillate tank. In either case the pressure on the delivery side of the condenser during the feed is atmospheric or only slightly above since the distillate tank is vented and the return line to the reducer is vented through the aniline water tank.

The reducer is lagged except for the ends and the flange connection in the middle.

Uncovered radiating surface of reducer	42 sq. ft.
Covered radiating surface of reducer	105 sq. ft.

Method of Operation

The initial charge in the reducer is 1,200 lbs. nitrobenzene, 260 lbs. iron borings, 65 lbs. ferrous chloride ($FeCl_2$) and sufficient aniline water to facilitate the introduction of the iron borings. All of these materials are at room temperature or thereabouts and no reaction seems to go on. Of course during the entire operation mechanical agitation is kept on.

The reaction is started by blowing steam into the charge. This brings the temperature up to the boiling point and starts the vapor coming over through the condenser. The reducer is now ready for the regular iron feed until the calculated quantity of iron has been fed. The iron is introduced into the reducer in batches of 65 lbs. At the time of introduction the reducer is vented to the atmosphere through the aniline water tanks. The vent is partially closed immediately after the iron feed and the pressure in the reducer rises slightly, varying from 1 in. to 5 in. of mercury. The temperature also rises and vapor, presumably water vapor with some admixture of nitrobenzene vapor, passes to the condenser. The condensed liquid returns to a sight box which empties through a valve into the reducer at the operator's option. The top of the sight box is vented to the atmosphere. The operator determines what pressure exists in the reducer by opening the connecting valve between the sight box and reducer. When the condensed liquid will run back into the reducer, the pressure has been reduced sufficiently to allow of an additional iron feed. The time between feeds is about 11 minutes and from 3 hours to 3 hours 15 minutes are required for the complete iron feed of 1,300 lbs. of iron.

The reduction period follows the iron feed. Steam is introduced at a slow rate. The heat of reaction and the heat from the steam drives the vapor to the condenser from which the liquid returns directly to the reducer. If the reduction does not proceed satisfactorily as determined by inspection of samples, additional iron and chloride are added. Reduction is generally finished in 3 hours, the reduction being considered complete when a sample shows no nitrobenzene.

The distillation is carried out by increasing the steam supply and running the condensed distillate to the distillate storage tank. In this process, the only apparent heat available for distilling off the aniline is the superheat in the incoming steam, since no heat is furnished by any reaction.

Aniline Reducer Iron Feed

OBSERVED AND CALCULATED QUANTITIES

Time	Rate G P M	Water Temperatures			B T U Per Min	Reducer Temperature		Remarks
		In	Out	Diff		Vapor	Distillate	
								Initial feed 1,200 lbs. N.B. 65 lbs. chloride 260 lbs. iron
8:30	23.5							
8:35	23.5							
8:35	23.5							
8:40	23.5	48° F.	52° F.	4.0° F.	705	171° F		Steam on 1000/Hr.
8:45	23.5	48	68.2	20.2	3,960	208	97° F.	Steam off
8:55	23.5	47	77.0	30.0	5,875	206	97	65 lbs. iron in
9:05	23.5	47.3	91.4	44.1	8,630	206	100	65 " " "
9:18	23.5	48.5	94.0	45.5	8,910	206	103	65 " " "
9:32	23.5	47.5	95.0	47.5	9,300	206	103	65 " " "
9:45	23.5	49.0	91.0	42.0	8,225	206	99	65 " " "
9:58	23.5	47.5	91.5	44.0	8,620	206	100	65 " " "
10:10	23.5	47.0	96.0	49.0	9,600	206	99	65 " " "
10:25	21.8	47.5	93.0	45.5	8,250	206	100	65 " " "
10:35	21.8	47.7	96.0	48.3	8,780	206	102	65 " " "
10:48	21.8	47.8	103	55.2	10,000	206	108	65 " " "
11:09	21.8	47.5	101	53.5	9,700	208	107	65 " " "
11:14	21.5	47.7	106	58.3	10,420	207	112	65 " " "
11:23	21.5	47.5	108	60.5	10,820	208	122	65 " " "
11:30	21.5	47.5	109	61.5	11,000	210	130	65 " " "
11:40	21.5	47.5	104	56.5	10,100	211	118	65 " " "
11:47	21.5	47.5	103	55.5	9,930	212	116	65 " " "
11:55	21.5	47.5	113	65.5	11,700	210	130	Blowing dephlegmator with steam 2 min. 1,000 lbs. hr.
Average					9,100	208	108	

(1) Total time iron feed period	3 hrs. 25 min.
(2) Actual time iron feed after initial charge	3 hrs. 10 min.
*(3) Total B.T.U. given up to water during iron feed	1,733,000 B.T.U.
(4) Average temperature of air	40° F
(5) Ave. temp. of reducer (vapor temperature)	208° F
(6) Average difference in temperature	168° F
(7) Estimated ave. rate of heat transfer of uncovered surface of reducer	2 B.T.U./hr./sq. ft./1° F.
(8) Estimated ave. rate of heat transfer of covered surface of reducer	.5 B.T.U./hr./sq. ft./1° F.
(9) Rate of heat loss through uncovered surface 42 × 2 × 168	14,100 B.T.U./hr.
(10) Rate of heat loss through covered surface 105 × 5 × 168	8,800 B.T.U./hr.
(11) Total rate of heat loss by radiation	22,900 B.T.U./hr.
(12) Heat loss by radiation during iron feed 22,900 × 3 1/6	72,500 B.T.U.
†(13) Total heat generated by reducer during iron feed (3) + (12)	1,805,000 B.T.U.
Initial charge in reducer:	
Nitrobenzene	1,200 lbs.
Ferrous chloride	65 lbs.
Iron borings	260 lbs.
Aniline water (estimated)	30 lbs.
Total charge in reducer at end of iron feed:	
Nitrobenzene	1,200 lbs.
Ferrous chloride	65 lbs.
Iron borings	1,300 lbs.
Aniline water (estimated)	250 lbs.

The full 1,200 lbs. of nitrobenzene does not, of course, exist at the end of the iron feed period. There is some aniline and perhaps some intermediate compounds.

It is estimated 7 lbs. of aniline water are introduced with each 65 lbs. iron feed. This accounts for 140 lbs. of water. The remainder is condensed steam as measured on the meter.

The average pressure in the reducer is 2 in. of mercury. The barometer was 29.5 in. Hg which makes the absolute pressure in the reducer 31.5 in. Hg. The boiling point of water at this pressure is 214.6° F. The observed temperature of the vapor from the reducer was 206° F. during the early part of the

* 9,100 B.T.U./min. × 3 hrs. 25 min.

† No heat delivered to reducer during feed, consequently 1,805,000 B.T.U. generated by reaction.

iron feed period, rising to 212° F. at the end. The temperature variations between iron feeds was less than a degree. It would rise and fall with the pressure.

Aniline Reducer—Reduction Period

OBSERVED AND CALCULATED QUANTITIES

Time	Rate G P M.	Water Temperature ° F.			Heat Rate B T U. Min.	Reducer Temp ° F.		Steam Gage	Lbs. Per Hr.	Remarks
		In	Out	Diff		Vap	Dist.			
12:05	28 6	47.7	102	54.3	9,420	210	111	115	210	Steam on
12:10	20.6	47.7	105.7	58	9,950	208	115	112	264	
12:20	20 6	47.7	106.7	59	10,130	208	116	105	240	
12:30	20.6	47.7	101.3	53.4	9,170	208	106	105	212	
12:40	20.6	47.9	97.9	50	8,580	207	95	102	347	
12:50	20.6	47.9	99.5	51.6	8,880	207	102	111	487	
1:00.	20.6	47.9	100.5	52.5	9,030	207	102	112	464	
1:10	20.6	48.0	99.5	51.6	8,860	208	105	111	454	
1:15	20.6	47.9	94	46.1	7,910	204	96			Steam off --130 lbs. iron in
1:19										Steam on
1:20	20.6	48.0	95	47	8,080	208	104	105	415	
1:30	20.6	48.0	98	50	8,600	207	104	113	496	
1:40	21.7	48 0	99.5	51.5	9,320	208	109	115	483	
1.50	21.7	48.0	97.8	49.8	9,010	208	120	118	311	7 lbs. chloride in
2:00	21.7	48 0	99	51	9,210	207	111	113	456	
2:10	21.7	48.2	130	81.8	14,840	207	108	118	484	
2:20	19.1	48.2	129	80.8	12,860	208	116	120	420	65 lbs. iron in
2:30	19.1	48 2	107	58.8	9,370	207	115	124	395	
2.40	20.5	48.2	102	53.8	9,200	208	103	118	493	
2:50	20.5	48.2	98	49.8	8,520	209	104	118	502	
3:00	20.5	48.4	102	53.6	9,180	208	122	120	322	
3:10	20.5	48.4	95	46.6	7,970	207	122	125	525	
Average					9,515	208	110	114	400	

(14) Heat taken out by water 9,515 × 3.083 hrs. × 60 min. 1,760,000 B.T.U.

(15) Heat given up by steam 400 × 3.02 (1,190) (avg. B.T.U. per lb. of steam)--(110 plus 32) ..... 1,343,000 B.T.U.

(16) Heat loss by radiation (12) × 3.083 .... 71,000 B.T.U.

(17) Total heat rejected by reducer (14) plus (16) ..... 1,831,000 B.T U.

(18) Total heat apparently furnished by reaction (17) minus (15) ..... 488,000 B.T.U.

(19) Water condensed by condenser (14) ÷ (1150.4 — 110 plus 32) .... 1,640 lbs. water

(20) Water introduced by steam 400 × 3.083 ..... 1,225 lbs. water

Total charge in reducer at end of reduction:

Aniline	900 lbs.
Water (1,225 plus 110)	1,335 lbs.
Iron	1,495 lbs.
Iron for chloride	28 lbs.
Iron sludge 1,523 × 232 ÷ 168	2,100 lbs.

It is assumed that the amount of aniline water introduced with the iron borings is equivalent to that returned to the aniline water tanks. This is very nearly correct since the operators add but little aniline water to the water tanks.

Aniline Reducer—Distillation Period

OBSERVED AND CALCULATED QUANTITIES

Time	Rate G P M	Water Temperature ° F			Water Heat Rate B T U	Reducer Temp ° F		Steam Gage	Lbs Per Hr	Remarks
		In	Out	Diff	Min	Vap	Dist			
3.14	27	48.2	99.5	51.3	11,500	210	160	123	943	Distillation on
3:20	27	48.4	106.7	58.3	13,100	212	165	123	953	
3:30	27	48.4	116.5	68.1	15,300	213	171	123	1,008	
3:40	27	48.5	123	74.5	16,750	213	170	126	985	
3:50	27	48.7	126.5	77.8	17,500	213	168	126	950	
4:00	27	48.8	123.7	74.9	16,850	213	169	128	935	
4.15	25	48.7	122	73.3	15,300	212	169	128	945	
4.30	25	48.5	121	72.5	15,100	212	170	126	940	
4:45	25	48.5	133.8	85.3	17,800	213	177	127	955	
5:00	25	48.5	125.7	77.2	16,100	212	160	118	943	
5.15	25	49.0	123	74.0	15,400	212	151	127	920	
5.30	25	49.3	126.5	77.2	16,100	212	153	127	960	
5:45	25	49.7	123	73.3	15,300	212	152	122	960	
6:00	25	49.7	121	71.3	14,900	212	154	123	965	
6.15	25.2	49.5	126.5	77.0	16,200	212	154	121	960	
6.30	25.2	49.5	122	72.5	15,200	212	154	127	980	
6:45	25.2	49.3	123	73.7	15,500	212	158	120	970	
7:00	25.2	49.5	122	72.5	15,300	212	160	114	930	
7:15	25.7	49.7	123	73.3	15,700	212	164	114	940	
7.30	25.7	49.7	123.7	74.0	15,900	212	166	116	973	
7.45	25.7	49.5	133	83.5	17,900	212	169	110	925	
8.00	25.7	49.3	123	73.7	15,800	212	166	114	960	
8.15	29.4	49.1	123.7	74.6	18,300	213	165	120	973	
8.30	29.4	49.0	124.7	75.7	18,500	213	165	122	988	First clear sample at 8:40
8.45	29.4	48.6	124.7	76.1	18,700	213.5	165	128	983	Dist. complete
Average					16,100	212.3	154	122	955	

Total time consumed 5 hrs. 31 min.

Inches in reducer 33 in.

Inches in distillation tank water 38 in.—aniline 6 1/2 in.

(21)	Heat taken out by water—16,100 × 331 min.	5,329,000 B.T.U.
(22)	Heat loss by radiation 23,200 × 5.52 hrs.	128,000 B.T.U.
(23)	Total heat rejected	5,457,000 B.T.U.
(24)	Heat furnished by steam 955 (steam lbs. per hr.) × 5.52 hrs. × 1,060 (B.T.U. per lb. of steam at line pressure)	5,585,000 B.T.U.
(25)	Heat unaccounted for (24) — (23)	128,000 B.T.U.
(26)	Percentage unaccounted for (probably moisture in steam)	2.3 percent
(27)	Heat available for aniline distillation 955 × 5.52 × (1,192 — 1,150)	221,400 B.T.U.
(28)	Used by aniline vaporization 900 × 205	181,500 B.T.U.
(29)	Heat unaccounted for as used in vaporizing moisture in steam	36,900 B.T.U.
(30)	Steam supplied during distillation 955 × 5.52 hrs.	5,275 lbs. water

Aniline Reducer—General Conclusions

Weight balance		
Materials supplied		
Steam:		
Reduction	1,335 lbs.	
Distillation	5,275 lbs.	
Total		6,610 lbs.
Iron		1,495 lbs.
Chloride		72 lbs.
Nitrobenzene		1,200 lbs.
Total		9,377 lbs.
Products:		
Aniline		900 lbs.
Water in still tank 38 in. at 135 lbs./inch		5,140 lbs.
Fe_3O_4 (by calculation)		2,100 lbs.
Water in reducer		1,300 lbs.
Total		9,440 lbs.

No sludge weights were obtained, but from previous tests the weight per inch of sludge in reducer is estimated at 103 lbs. Number of inches in reducer = 33. Weight of Fe_3O_4 by calculation from iron borings and iron in chloride is 2,100 lbs. and the remainder of the weight is considered as water.

Some water is used in the reaction but no practical way of measuring this amount could be found. The amount by calculation is about 175 lbs. (on a hydrogen basis) but no doubt this figure is not representative of what is going on. The oxygen content requires about 260 lbs. of water if all iron goes to Fe_3O_4.

Summary:

Pressure in reducer during iron feed	.2 in. Hg.
Pressure in reducer during reduction	.5 in. to 1 in. Hg.
Pressure in reducer during distillation	.5 in. to 1 in. Hg.
Barometer during test	29.5 in. Hg. (corrected for temp.)

Steam used:

Heating original charge and blowing dephlegmator	110 lbs.
During reduction	1,225 lbs.
During distillation	5,275 lbs.
Total	6,610 lbs.
Steam constant 6,610/900 – in reducer house	7,350 lbs./1,000 lbs. of aniline

Water used	17,350 Gals.
Water constant	19,300 G./M.
Water rate per reducer in operation	23.6 G.P.M.
Heat liberated by reduction (13)+(18)	2,293,000 B.T.U.
Heat of conversion nitrobenzene to aniline, per lb. aniline	2,548 B.T.U.
Heat of conversion nitrobenzene to aniline, per lb. nitrobenzene	1,911 B.T.U.

Aniline reducer

Comments on Operation

Iron Feed Period

Immediately after the iron is fed into the reducer the pressure rises slightly and no more iron is introduced until the pressure drops to .5-1 in. Hg. The pressure rise is due to the formation of free hydrogen and steam. The steam is condensed but the hydrogen formed passes out through the vent. It appears that when the water supply is scant the pressure falls less rapidly and the iron feed is delayed. When the water supply is ample the condensation is facilitated and the condensate returns to the reducer cold. The heat taken up by this returned condensate helps to reduce the pressure rise on the next iron feed and the rate of feeding iron is therefore increased. It appears from the foregoing that it is not advisable to try to reduce the water rate. Water is the only form of power used except that required for agitation.

Reduction Period

The reduction requires the use of steam. All vapors that are driven off are condensed and returned to the reducer. It

appears that a low temperature of the condensate is not desirable since it means that more steam is necessary to reflux the materials properly. It is customary for the reducer operator to throttle the water supply to the condenser at this period.

Distillation Period

It is quite evident that the only heat available for distilling off the aniline is that contained in the superheat of the steam, since steam when introduced into a solution will not condense after the boiling point of the solution has been reached. Steam in expanding from 120 lbs. to atmosphere develops 42 B.T.U. in superheat per lb. (neglecting moisture in steam). On the above basis it seems that by superheating the steam fed into the reducer the net steam required during the distillation period would be reduced, the time for distillation would also be reduced and, furthermore, less water would be delivered to the distillation house. However, in view of the fact that this method of steam distilling the aniline charge is not looked upon very favorably, the installation of any superheating equipment would not be advisable.

Steam Consumption—Aniline Rectifier

In order to determine the thermal efficiency of the aniline rectifier, a test run was made, in which the condensed steam used in the coils was accurately weighed. During the entire run the essential data bearing on the operation were tabulated.

The method of obtaining the steam used was as follows: The steam from the trap was led through an iron coil immersed in a cooling bath. The hot water from the coils was then piped into an oak barrel placed on a scale. A valve separated the coil from the barrel in order that the flow could be stopped while the barrel was being emptied by means of a wooden plug at its base.

It is interesting to record the theoretical calculations for the amount of steam necessary to distill aniline, and compare the results with the actual figures obtained.

Steam Required to Distill Aniline

Average temperature of crude oil delivered to rectifier ...	80° F.
Boiling point maintained at 28″ vacuum	230° F.
Difference in temperature—sensible heat	150°
Specific heat of aniline	×.52
	78.0 B.T.U.
Latent heat of vaporization	180.0
Reflux in dephlegmator 1/3 latent heat (est.)	60
Total B.T.U. required per pound of aniline	318.0 B.T.U.
Latent heat of steam supplied at 140 lbs. pressure	860 B.T.U.

$\frac{860}{318} = 2.70$ lbs. of oil distilled per lb. of steam used.

$\frac{31,800}{860} = 37$ lbs. of steam required per 100 lbs. aniline.

Of course it would be necessary to make slight corrections for losses by radiation.

In the following test the results show that the steam consumption per 100 lbs. of aniline was 52, 52, and 38 lbs. respectively for the three tanks. The greater efficiency of the last scale can only be accounted for by not having so great a reflux in the dephlegmator towards the end of the run. In fact, the high figure 1.83 for the lbs. of steam necessary to drive off the water at the beginning of the run is also probably due to the great reflux action at the start of the run. If absolutely no reflux action took place in the dephlegmator, then 30 lbs. of steam would distill 100 lbs. of aniline or 3 1/3 lbs. of aniline would be distilled per pound of steam.

Disregarding all theoretical considerations, we find that 18,000 lbs. of steam was used to distill off 23,440 lbs. of pure rectified aniline. This would give 77 lbs. of steam as the actual figure for rectifying 100 lbs. of aniline.

Calculations Involved in Water Stage

Weight of charge	27,300 lbs.
Containing	25,350 lbs. aniline 1,950 lbs. water

Initial temperature	80° F.
Water off at	120° F.
Good aniline	225° F.

B.T.U. Required to bring charge up to boiling:

(25,350 × 145 × 0.5) = 1,837,880 B.T.U. for aniline
(1,950 × 45 × 1.0) = 87,750 B.T.U. for water
1,925,630

B.T.U. available per lb. of steam at 140 lbs. pressure = 860

$$\frac{1,925,630}{860} = 2,204 \text{ lbs. steam consumed in bringing charge up to boiling point.}$$

Heat lost by radiation—415 lbs. (431 sq. ft × 8 hrs. × 12).
Heat lost by dephlegmator—415 lbs.
Total heat expended in bringing system to boiling point ..... 3,034 lbs.
Total steam used during water stage ..... 6,900 lbs.
∴ Steam used for actual evaporation ..... 3,866 lbs.

Steam per lb. aniline water $\frac{3,866}{2,700}$ — 1.43 lbs.

Steam needed for 750 lbs. aniline = 390 lbs. at 52 lbs. steam per 100 lbs. oil.
Steam needed for 1,950 lbs. water = 3,476 lbs. at 178 lbs. steam per 100 lbs. water.
Steam needed for 2,700 lbs. aniline water (see below) = 3,866 lbs. (390 lbs. + 3,476 lbs.).

Aniline Rectifier

STEAM CONSUMPTION—WATER STAGE

Time P M	Elapsed Time	Temp Rectifier	Temp Dephleg	Vacuum	Steam Used	Weight of Aniline Water Distilled
12:03		85° F.		25		
12:22	19 min.	103	100° F.	27¾	300 lbs.	2,700 lbs. aniline water
12:43	19	117	110	27¼	300	
1:01	18	123	122	27	300	1,950 lbs. water
1:19	18	132	127	26½	300	750 lbs. aniline
1:35	16	130	130	26¼	300	Total steam condensed 6,900 lbs.
1:53	18	137	130	26	300	
2:13	20	142	130	25½	300	
2.37	24	145	130	25½	300	Time elapsed 8½ hrs.
3:00	23	150	130	25½	300	Av. rate of distillation 318 lbs. per hour
3:24	24	155	130	26	300	
3:45	21	159	133	26	300	
4:07	22	165	133	26½	300	
4 30	23	165	133	27	300	
5:00	30	165	115	27½	300	Cooled rectifier trifle too hot
5:25	25	180	115	27¼	300	
5.45	20	185	115	27¼	300	
6:06	21	195	115	27	300	
6:27	21	203	115	27	300	
6:50	23	210	115	27½	300	
7:10	20	215	115	28	300	
7:35	25	220	120	28	300	
8:05	30	225	150	28½	300	
8:30	25	225	195	28½	300	

Aniline Rectifier

STEAM CONSUMPTION—ANILINE STAGE

First Tank

Time P.M.	Elapsed Time	Temp. Rectifier	Temp. Dephleg	Vacuum	Steam Used	Oil Distilled	Scale Weights
8:55		225° F.	205° F.	28″	300 lbs.		
9:20	25 min.	225	205	28	300	500 lbs.	500 lbs.
9:45	25	225	205	28	300	600	1,100
10:15	30	225	205	29	300	750	1,850
10:40	25	225	205	29	300	550	2,300
11:05	25	225	205	29	300	600	2,900
11:30	25	225	205	29	300	850	3,750
12:00	30	230	206	29	300	910	4,660
12:30	30	230	205	29	300	800	5,460
12:55	25	230	205	29	300	580	6,040
1:30	35	225	205	29	300	660	6,700
1:55	25	225	205	29	300	550	7,250
2:25	30	225	200	25	300	190	7,440
							Empty tank

Totals 5 hrs. 30 min. 3,900 7,440

Rate distillation per hour .. .. 1,350 lbs.

Steam per 100 lbs. aniline $\frac{3,900}{7,440}$ .... 52 lbs.

Heat transfer 75 B.T.U. per sq. ft., per hr., per deg. diff. in temp.

Aniline Rectifier

STEAM CONSUMPTION—ANILINE STAGE

Second Tank

Time P.M.	Elapsed Time	Temp Rectifier	Temp Dephleg	Vacuum	Steam Used	Aniline Distilled	Scale Weights
2:50	25 min.	225° F.	200° F.	28″	300 lbs.		
3:20	30	225	200	27	300	500 lbs.	500 lbs.
3:50	30	225	200	29	300	750	1,250
4:15	25	225	200	29	300	550	1,800
4:40	25	225	200	29	300	450	2,350
5:05	25	225	200	29	300	450	2,800
5:30	25	225	200	29	300	630	3,430
5:55	25	225	200	29	300	570	4,000
6:25	30	225	200	29	300	650	4,650
6:50	25	225	200	29	300	750	5,400
7.20	30	223	200	29	300	700	6,100
7:45	25	224	198	29	300	750	6,850
8:10	25	223	198	29	300	700	7,550
8:33	23	223	198	29	300	450	8,000

Totals 5 hrs. 43 min. 4,200 8,000

Rate of distillation per hour ..... 1,400 lbs.

Steam per 100 lbs. aniline $\frac{4,200}{8,000}$ ..... 52 lbs.

Heat transfer 76 B.T.U. per sq. ft., per hr., per deg. diff. in temp.

Aniline Rectifier

STEAM CONSUMPTION—ANILINE STAGE

Third Tank

Time P M	Elapsed Time	Temp. Rectifier	Temp. Dephleg	Vacuum	Steam Used	Aniline Distilled	Scale Weights
8:52	25 min.	222° F.	178° F.	27″	300 lbs.		
9:22	24	224	198	29	300	1,700 lbs.	1,700 lbs.
9:47	25	230	205	29	300	740	2,440
10:09	20	200	200	29	300	860	3,300
10:29	20	224	200	29	300	800	4,100
10:49	20	224	199	29	300	780	4,880
11:09	20	224	198	29	300	700	5,580
11:30	21	224	198	29	300	800	6,380
11:52	22	225	197	29	300	820	7,200
12:18	26	225	197	29	300	800	8,000

Totals 3 hrs. 26 min. 3,000 8,000

Rate of distillation per hour .. .. 2,300 lbs.

Steam per 100 lbs. aniline $\frac{3,000}{8,000}$..... .... 38 lbs.

Heat transfer 90 B.T.U. per sq. ft., per hr., per deg. diff. in temp.

Finishing Lot

1:17 2:17	60 min.	228° F. 215	202° F. 150	29″ 29	300 lbs.	740 lbs.	740 lbs.

Steam per 100 lbs. aniline $\frac{300}{740} = 40$ lbs.

700 lbs. over in 20 minutes comparatively no steam being discharged when flow stopped

CHAPTER X

ANILINE POISONING

Previous to the outbreak of the Great War in 1914 the term "Aniline Poisoning" had little significance for the American medical profession and physicians in the United States gave its treatment practically no consideration. The exigencies of war and the subsequent development of dye industry here soon brought this unusual malady to the attention of physicians attached to large chemical plants and to the nearby hospitals.

No better review of the subject can be given than to quote from the quite comprehensive paper (delivered by Geo. P. Adamson at the meeting of the American Chemical Society in New York City, September, 1916) on "Industrial Poisoning from Aniline and Allied Products" prepared by the foremost American authorities on the subject. From an operating viewpoint the loss of time due to the poisonous effects of aniline and its consequent lowering of the morale among the workers presents a serious problem. The first symptom guiding supervisors in the handling of workers is the blue coloration of the lips and finger tips due to cyanosis. The immediate effect of the absorption of the poison is to cause a severe headache and give rise to a high pulse which often rises above 100. The calves of the legs become very weak and the patient experiences difficulty in walking.

Realizing that poisoning may be caused by absorption through the skin, by direct contact or by saturation of the clothing, through the digestive organs, or through the respiratory as volatile particles, the manufacturing precautions and preventative methods have been based on these facts. The aniline buildings are consequently constructed embodying the best ventilating features. Large suction fans to which are connected ducts coming from above the operating machines are installed in ante-buildings and serve to exhaust any poisonous fumes and to create a circulation of fresh air. In addition to this, individual fans for

each operator are placed at open windows. The manufacturing system is kept closed and the technique arranged to eliminate any handling in the open. Drinking men are excluded from the operating force. Regular rations of milk, clean uniforms, leather gloves, and rubbers or boots are usually provided for the men. Shower baths are installed and their daily use is insisted upon. Vinegar baths where employees can bathe the hands, face, and upper part of the body are provided and the men are required to use this ablution daily, under supervision.

The necessity of replacing the stirring plows in the aniline reducers is the cause of many of the poisoning cases observed; for in spite of continued washing and steaming out of the machines, there is sufficient aniline saturating the residual iron borings in the reducer bottom to make it inadvisable for men to remain in the reducer more than ten minutes at a stretch, or one hour for the entire day. When operators are in the reducers they are provided with an air helmet which keeps a supply of fresh compressed air going through the helmet case. After the reducer is cleaned the men immediately take a shower bath and a vinegar bath, and are not permitted to do any other work for that day. A rest period of two hours is then insisted upon, during which time any symptoms of poisoning may be observed. During the summer months, employees engaged in cleaning reducers are not permitted to walk in the strong sunlight and are conveyed home.

Blood Examinations on Aniline Operators*

Twenty men were examined, and full blood counts made; seven of them were examined in 1915 and again in 1916. The other thirteen continued to work in aniline but a short time after the first examinations were made and, unfortunately, we cannot draw any definite conclusions from our examinations of them. We also examined specimens from twelve men under the spectroscope, to see if any trace of methemoglobin could be detected by this means. Spectroscopic examinations were all

* Paper by Francis S. Chambers, M.D.

made about five p.m. after the men had been working for some hours; a few showed slight blueness of the lips, but no other symptoms. In no instance did we detect any traces of methemoglobin.

Regular full blood counts were made in all instances, consisting of hemoglobin estimations with Dare's instrument, counts of the red cells (erythrocytes) and also of the white cells (leucocytes). Smears were prepared in the usual way and examined with Wright's stain. We noticed that the most frequent change was a slight anemia, characterized by a reduction in the hemoglobin and a fall of the red cell count. Thus in the men who were examined in 1915 and again in 1916, four showed such changes. The first examinations on these four men were made shortly after they began to work in aniline.

Full Blood Counts

No.	Hemoglobin			Erythrocytes			Leucocytes	
	1915	1916	Loss	1915	1916	Loss	1915	1916
1	94	85	9%	5,800,000	5,040,000	13%	9,000	6,200
2	95	87	8%	5,520,000	5,000,000	20%	9,100	10,000
3	90	80	11%	5,900,000	4,408,000	25%	8,000	7,200
4	80	70	12%	5,200,000	4,600,000	11%	9,400	8,000
5	87	88		4,440,000	4,240,000		7,250	8,200
6	70	82		4,880,000	4,152,000		6,600	5,800
7	78	90		6,000,000	5,968,000		6,100	6,200

No. 2. Increase of polymorphonuclears and reduction of small mononuclears; this may be due to some foreign causes.

No. 4. The red cells also show some variation in size, about five to eight microns. No nucleated reds present.

No. 5. Some variation in the size of the red cells, about six to eight microns.

No. 6. Was an old employee when first examined, and this is the probable cause of the increased number of small mononuclears, in 1915. His hemoglobin shows an increase on second examination, and with the reduction of the number of small mononuclears, his blood has somewhat improved. His first examination was made before the shorter hour shifts were adopted.

No. 7. Had been working in aniline for some time before the first blood count was made and this is the probable reason that the differential count shows no changes. His hemoglobin shows an increase.

Differential Count of Leucocytes

No	Polymorphonuclears		Small Mononuclears		Large Mononuclears		Transitional Forms		Eosinophiles		Basophiles	
	1915	1916	1915	1916	1915	1916	1915	1916	1915	1916	1915	1916
1	5,940	3,286	2,880	2,666	90	62	0	124	90	62	0	
2	5,642	7,700	3,003	2,100	91	0	91	100	273	100		
3	4,560	4,104	2,560	2,592	480	216	0	144	400	72	0	72
4	7,308	4,320	2,162	3,440	282	80	376	80	188	80	0	
5	4,464	3,936	2,016	3,116	360	738	144	164	216	246	0	
6	3,432	3,364	2,904	1,740	66	348	66	116	132	242	0	
7	3,294	3,186	2,135	2,601	183	124	183	None	305	186	0	
				*	*Percentages*							
1	66	53	32	43	1	1	0	2	1	1	0	
2	62	77	33	21	1	0	1	1	3	1		
3	57	57	32	36	6	3	0	2	5	1	0	1
4	68	54	23	43	3	1	4	1	2	1	0	
5	62	48	28	38	5	9	2	2	3	3	0	
6	52	58	44	30	1	6	1	2	2	4	0	
7	51	53	35	42	3	2	3	0	5	3		

Of the thirteen men who were examined once, four were men who had been working in aniline for some time before the examinations were made, the other nine were new applicants for positions in the aniline department. Of these four men, three show rather poor amount of hemoglobin; the percentages are lower than in the other thirteen men. No. 8 had some pulmonary disease and his low percentage of hemoglobin was not entirely, if at all, due to aniline.

Three men did not show a reduction in hemoglobin after working over a year in aniline, two show an increase. These men had been working in aniline for some time prior to the first examination, and subsequently shorter hours of work were adopted which may account for their improvement.

The leucocytes showed no abnormal variations. In the dif-

* Read across page to obtain percentage of each class for each individual.

ferential count of the white cells, a reduction in the polymorphonuclears and an increase in the small mononuclears, both relative and absolute, were observed in two (Nos. 4 and 5). In the others, the variations were not great, although many of the men showed a relatively high small mononuclear count.

The chief change of importance is in the percentage of hemoglobin and the number of red cells, long continued exposure to aniline causing a reduction in both elements. While it is desirable to have some idea of the condition of the blood of these men, it is not always practicable to have a repeated full blood count made, owing to the time, expense and fear which it arouses in the men. Frequently the men seek other occupations for this reason.

However, it is desirable to have an estimation of the hemoglobin made on all men seeking employment in the aniline department, and if same is found to be below 85 percent, the applicant had better be rejected. For this purpose, the Fleischel instrument of Dare's hemoglobinometer can be employed by an intelligent person with a little practice.

Subsequent examinations should be made at intervals of three or four months or in special instances, when an employee looks badly, more frequently. If the hemoglobin falls below 75 percent he should be kept under observation and if it should fall below 70 percent, he should be advised to seek other employment.

In all doubtful cases, a full blood count should be made. Obviously, blood examinations do not offer any protection against acute poisoning, but they do enable a better selection of men suitable for this work.

Symptoms of Poisoning

ACUTE: (*a*) *Mild Cases.*—Pallor of skin and mucous membranes, with slight cyanosis; a feeling of weariness and weakness; head symptoms, vertigo, reeling, unsteady gait; deficient elasticity of movement; slow, labored speech; irritability (aniline "pip"); condition of slight inebriation, with loquacity,

gaiety and defective power or orientation; loss of appetite, constipation and tense rapid pulse.

(*b*) *Severe Cases.*—Dark blue to swarthy cyanosis; formation of methemoglobin; bounding pulse; "air hunger" with great frequency of respiration; lowering of sensibility; obliteration of reflexes; sometimes vomiting, strangury and bloody urine.

(*c*) *Most Severe Cases.*—Sudden prostration; cold, pale skin, blue lips, nose and ears; diminution and even extinction of sensibility; moist, cold skin, small pulse; death in a comatose condition, sometimes after antecedent convulsions.

SUB-ACUTE AND CHRONIC.—Anemia; slowing of the pulse; disorders of digestion, such as eruptions, loathing of food, vomiting, diarrhea and eczematoris and pustular eruptions on various parts of the body, especially on scrotum; nervous symptoms, as general debility, headache, ringing in the ears, vertigo, unrestful sleep, disturbances of sensibility, often of morility; spasmodic muscular pain. This form of poisoning is rare. Anemia and retarded pulse are early symptoms. The blood is of brownish hue but microscopically unchanged; occasionally the urine contains blood.

Treatment

At the first symptoms of poisoning, immediate removal from work room to cool shady spot, change of clothing, cool effusions, administration of oxygen in connection with artificial respiration; latterly the pulmotor has met this emergency with great success; in severe cases, blood letting with subsequent infusion of physiological salt solution; copious ingestion of milk; in weak action of heart, stimulate (black coffee, camphor, ether, but no alcohol). Caution against the use of alcohol during and immediately after labor; abstinence is advisable. Treatment, however, is entirely symptomatic and expectant. Immediate removal of all marked cases to hospital or other well-equipped domicile is recommended.

MALIGNANT TUMORS OF THE BLADDER IN WORKERS IN THE ORGANIC CHEMICAL INDUSTRY *

Malignant tumor (cancer) of the bladder occurs as an occupational disease among workers who come in contact with aniline vapors. The occurrence of this disease among workers engaged in the manufacture of benzidine is probably due to the aniline, 4 to 5 percent of which is formed as a by-product. The disease is produced only if the aniline be inhaled as a highly diluted gas; solid benzidine did not produce diseases of the bladder when introduced in the dry powdered state into the digestive canal and the respiratory tract. The workmen attacked by the cancer have not been engaged in evaporation or distillation of pure benzidine, but have been employed in adjoining buildings of the factory or in the open air, and have inhaled the aniline vapors highly diluted with air. The poison, inhaled in very small amounts, is dissolved in the moisture of the alveoli, and enters the cells and the lymph or blood streamswithout producing direct symptoms of intoxication. Since aniline is comparatively easily soluble in water to a 3 percent solution, while benzidine is scarcely soluble in water and quite insoluble in the salt-containing fluids of the cells, aniline and not benzidine must be the poison. Moreover, tumor of the bladder has not been noted among workmen who have been exposed for 20 and more years to extremely fine dust of aniline-free benzidine. The poison is oxidized or otherwise altered in the animal body, and the products are excreted, in part, by the feces, urine and perspiration; however, a portion of these products remains in some, as yet undetermined, part of the body, and after the lapse of time, attains a certain threshold, and stimulates the epithelium of the bladder to the formation of new cells and malignant growth. A workman may be employed on the average for 16 years before the first symptoms of the disease appear. Of the operations for tumors of the bladder made at a surgical clinic of the University of Frankfurt during a period of 23 years, from 25 to 30 percent were

* MAX NASSAUER. Frankfurt a/M. Z. Angew Chem. 32, I, 333-5 (1919).

for tumors produced by aniline. The prophylaxis is divided into factory construction and personal hygiene."

Paranitroaniline Poisoning

Paranitroaniline poisoning is similar to that of aniline, only much more acute. The patient here takes on a yellowish pallor and becomes generally weak even during quite normal operations. There is a distinct disintegration of muscular fiber which leaves the operator in poor physical condition. The tendency to constipation is quite marked and workers make a practice of indulging in laxatives. Continued service in paranitroaniline manufacture, particularly when the material is made from paranitrochlorobenzene, causes the system to become so run down that even the genital organs fail to function properly. Several cases were followed up and microsocopic tests showed that although there was an abundant production of well-formed spermatozoa, these were all quite immobile and incapable of functioning in the fertilization process. The patients in these cases were all given a vacation and instructed to exercise systematically in the open air. A month of relaxation and healthful exercise brought about a healthy condition of the genital organs along with a rejuvenated feeling on the part of the workers.

CHAPTER XI

SOME PHYSICAL CONSTANTS OF PURE ANILINE *

The importance of aniline to the dye industry has long been recognized, but no practical method of analysis has been available for general use in judging its quality. An attempt has therefore been made to find a method of analysis or test which would not only be accurate, but of such a nature that it could be applied quickly and easily in the control of the manufacture of this product.

A survey of chemical methods of analysis disclosed the fact that due to the rather large experimental errors, most of them fail when the purity of the aniline exceeds 99.5 percent. Attention was therefore turned to the possibilities of the application of the physical constants for accurately judging the purity. It would naturally be expected that the physical constants of such a common intermediate would long since have been established beyond any reasonable question. As a matter of fact, a great number of investigators have made a study of aniline but, instead of establishing these points, widely diverging results have been published.

On consulting the literature, no less than 16 different values for the freezing point of aniline were found. These vary between —8° and —5.96° C., where values for the boiling point ranged from 182.5° to 184.8° C. Of the numerous results given, the only ones considered were those in which the method of purification and methods of recording temperatures were fully described. The following have been chosen as most reliable, and are those generally accepted: Ampola's freezing point of —5.96°, Timmermans' —6.20° and that of Jones and Sanderson of —6.00° C. The latter has been published since the completion of this work, along with a formula for determining the purity of aniline from its freezing point. Timmermans, Callender, and Beckmann

* Paper by C. L. Knowles, presented to A. C. S., St. Louis, 1920. Courtesy E. I. DuPont de Nemours & Co.

apparently give the most accurate boiling points, their results being 184.40°, 184.10° and 184.30° C.

Since no conclusions could be drawn from these results, it was necessary to prepare a sample of pure aniline, and to determine accurately its physical constants. In the course of this work it was soon discovered why so many different values had appeared for the physical constants of aniline, since to purify aniline and maintain it in a pure state was found to be a matter of considerable difficulty.

Preparation of the Sample

Two liters of colorless aniline were distilled in vacuo four times, rejecting the first and last portions in each case. The product thus obtained was allowed to drop slowly into a saturated solution of recrystallized oxalic acid. The aniline oxalate was filtered off, washed several times with water, and three times recrystallized from 95 percent ethyl alcohol. The salt was washed with pure ethyl ether after each crystallization. In order to regenerate the aniline, a saturated solution of recrystallized sodium carbonate was added, the aniline distilled off, and distilled in vacuo three more times. When possible, determinations were made immediately on the sample. When this could not be done, the material was kept in a darkened vacuum desiccator.

Determination of Physical Constants

Boiling Point.—For the boiling-point determination a standard Beckmann boiling-point apparatus was used, readings being taken by means of a platinum resistance thermometer. This apparatus had been recently standardized by the U. S. Bureau of Standards for three points: for ice, the boiling point of water, and the boiling point of sulfur. The manufacturers guaranteed an accuracy of 0.01°. Before and after each determination the thermometer was further checked against the ice point and freezing point of benzene. It is of interest to note that we were able to check very well the freezing point of benzene, obtaining

5.486° C., as compared with 5.493° C. = 0.007 as obtained by Richards.*

Following all precautions mentioned later, we obtained consistently a boiling point of pure aniline of 184.32° to 184.39° C. at 760 mm. pressure.

Freezing Point.—Immediately after vacuum distillation, the pure sample (10 to 15 cc.) was transferred to a test tube surrounded by a larger glass tube, and supported at the top by a thin ring of asbestos. The platinum resistance thermometer and a stirrer were inserted, and the whole immersed in a brine mixture at —10° to —12° C. The sample was stirred at a uniform rate and the freezing point determined. It was found to be —6.24° C., consistent checks being obtained.

Specific Gravity.—Specific gravity determinations were made on the freshly distilled sample in a pycnometer at 15° C., and compared with water at the same temperature, giving a value of 1.0268 at 15°/15° C.

Refractive Index.—The index of refraction was determined by means of an Abbe refractometer, manufactured and calibrated by the Zeiss Instrument Co. The best samples of aniline had an index of refraction of 1.5850 at 20° C.

Precautions Observed.—Numerous articles have been published in reference to the effect of air and light on aniline. While this phase of the subject is of great interest, it is manifestly beyond the scope of this paper. It has been noted that the purer the sample of aniline the more stable it is toward air and light. Our purest samples have darkened but slightly when kept in diffused light for months.

Effect of Moisture.—One property of aniline which caused considerable trouble in our work, and which apparently has received but very little attention in the past, is its extreme hygroscopicity. It is believed that this alone accounts to a large extent for the conflicting results found in the literature. If aniline in the pure state be exposed to the air for but one hour, the freezing point and boiling point are materially affected;

* Z. physik. Chem., 12 (1893), 433.

consequently extreme care must be taken in determining constants of the pure material. If undue time is required for these determinations, no accurate figures can be obtained. For this reason all samples were freshly distilled in vacuo, and determinations made as rapidly as possible. In order to check these results, attempts were made to determine freezing points in vacuo, but due to the mechanical difficulties encountered, no results of value were obtained. Results of both freezing-point and boiling-point determinations made in an atmosphere of dry inert gas, such as nitrogen or carbon dioxide, were identical with those of determinations made rapidly in the presence of air. In order to clearly demonstrate the effect of moisture on the purity of aniline, freezing points were made hourly on a sample exposed to the air. The initial freezing point was —6.35° C., after 1 hour it had fallen to —6.60° C., after 16 hours it was —7.30° C., and after 46 hours a freezing point of —8.20° C. was obtained. Assuming the formula for water at 0° C. to be $(H_2O)4$, this represents 2.4 percent water absorbed, based on the molecular weight of water as 18, the amount of water present becomes 0.6 percent.

The effect of entrained air and diminished pressure on freezing points has been carefully studied by Richards. He concludes that the error due to vacuum is practically negligible, as is also that due to dissolved air in the case of benzene.

Discussion of Results

The following have been chosen as the most reliable of previous freezing-point determinations:

	Year	Freezing Point °C
Ampola and Rimatori	1897	- 5.961 *
Timmermans	1911	--6.202 †
Jones and Sanderson	1920	- 6.003 ‡

* Gazz. chim. ital. (1), *27*, 35.

† Bull. soc. chim. belg., *25* (1911), 300.

‡ J. Soc. Chem. Ind., *39* (1920), 87.

For boiling points the following appear fairly reliable:

	Year	Boiling Point °C
Callender	1899	184.10 §
Timmermans	1911	184.40 //
Beckmann	1914	184.39 ¶

Ampola and Rimatori purified their samples of aniline by repeated freezing out of the material. A repetition of their work gave in all cases a freezing point considerably lower than —6.24° C. The only explanation we have to offer is that their Beckmann thermometer might have been in error. The use of the Beckmann thermometer is considered bad practice for accurate work of this kind, since the standardization is difficult and the stem correction excessive.

Timmermans' determinations were made on carefully purified aniline; measurements being made by means of a platinum resistance thermometer have been able to check these results fairly well.

Jones and Sanderson purified their samples by crystallization, followed by drying and distillation over caustic soda. Temperature measurements were made by means of a mercury thermometer and the freezing point of pure material calculated. We have carefully repeated this work, but failed to get a freezing point as high as that given in their report. As an alternative to the method of purifying aniline by formation of the oxalate, it has been found that repeated vacuum distillation gives material of the same freezing point. Samples prepared from recrystallized acetanilide were not of a high degree of purity.

Value of Freezing-Point Determination

In comparing the chemical analysis and physical constants of a large number of samples of aniline, it has been noted that the freezing-point determination is by far the best criterion of its purity. This method is being used in this laboratory to determine the purity of commercial samples of aniline.

§ Phil. Mag. (5), 48 (1899), 519.
// Bull. soc. chim. belg., 25 (1911), 300.
¶ Z. physik. Chem., 89 (1914), 112.
† Loc. cit.

By chemical analysis it has been shown that the impurities most frequently found in aniline are nitrobenzene, toluidine and water, these being present in most samples tested in the ratio 2 : 4 : 10.

In order to have available a short expression for converting the freezing point of a sample directly to purity, use has been made of the plan described by Jones. However, it will be noted that the figures used are different, due to the difference in freezing points of the pure samples of aniline upon which the expressions have been based. Jones * determined the impurities present and assumed an average molecular weight for them. Substituting this value in the cryoscopic molecular weight formula he obtained a simple expression in which the freezing point may be substituted directly, giving the percent aniline in the sample. Assuming 82.67 to be the average molecular weight of the impurities, the following formula may be used:

$$X = 108.79 \text{ plus } 1.41t.$$

where X = percent aniline present in the sample, and t = the observed freezing point in degrees C.

In developing this formula it was necessary to accept the cryoscopic constant of Ampola (5,870). Should this be slightly in error, the discrepancy in the result will be practically negligible. This is also the case when the relation of impurities is altered.

Summary

1. It is believed that the following are the true physical constants of aniline:

Freezing point	− 6.24° C.
Boiling point	184.32°, 184.39° C. at 760 mm.
Specific gravity (15°/15° C.)	1.0268
Refractive index (20° C.)	1.5850

2. The indications are that the freezing point is the best criterion of the purity of aniline.

3. In order to calculate the purity of a sample of aniline from its freezing point, use should be made of the formula:

$$X = 108.79 \text{ plus } 1.41t.$$

* J. Soc. Chem. Ind., 39 (1920), 8t.

CHAPTER XII

GENERAL CHEMICAL AND PHYSICAL DATA

Analyses Commercial Aniline

Pure aniline prepared by repeated vacuum distillation before and after conversion into the oxalate was found to have the following physical constants. (See previous chapter.)

Boiling point	184.32 — 184.39° C.
Freezing point	—6.24° C.
Specific gravity	1.0268 @ 15/15° C.
Refractive index	1.5850 @ 20° C.

An analysis of a commercial water-white aniline showed the following physical constants:

Boiling point	184.33° C.
Freezing point	—6.30° C.
Specific gravity	1.0270 — 15/15° C.
Dist. range	0.4° C.

Calculating the purity from the observed freezing point, this material is 99.91 percent pure.

Analysis of several commercial products on the market during 1919 gave the following results.

Source	Boiling Point	Freezing Point	Specific Gravity	Dist Range	Purity Chem Analysis	Purity from F. Pt	C_6H_5NO	Color
Standard from aniline oxalate	184.32	−6.24	1.0268			100.00	None	Colorless
A	184.35	−6.48	1.0269	0.1° C	99.9	99.7	Trace	Colorless
B	184.33	−6.30	1.0270	0.1° C	99.9	99.91	Trace	Colorless
C	184.08	−6.60	1.0274	1.5° C.	99.69	99.50	0.11	Colorless odor of H_2S
D	184.08	−7.20	1.0275	1.0° C	99.9	98.64	0.21	Dark brown
E	183.89	−8.10	1.0265	7.0° C.	99.6	97.73	0.10	Dark brown
F	184.35	−7.25	1.0260	5.5° C.		98.57	0.8	Red

Purity calculated from freezing-point depression:

$$X = 108.79 + 1.41T,$$

where

X = purity,

T = observed freezing point.

Determination of Aniline in Aniline Sludge

Mix the sample to be analyzed very well. This is very necessary, since it is very difficult to obtain a uniform sample of a sludge. Weigh out a 40 to 100 gram sample into a 1 litre round bottom distilling flask. To this add a sufficient amount of 5 percent NaOH solution so that the solution is slightly alkaline, after it has washed the sludge thoroughly. Connect to a steam still and distill over 300 cc. Place this distillate in a litre flask, add 50 cc. of concentrated HCl and then dilute to 1,000 cc. Place 100 cc. of this solution in a beaker, add 10 cc. of concentrated HCl and 5 grams of KBr. Titrate the solution with standard $KBrO_3$. The end point is reached when one drop in excess of the $KBrO_3$ after standing two minutes will enable one drop of the titrated solution to turn a KI test paper blue.

Calculation:

% Aniline =

$$\frac{\text{Aniline Value of } KBrO_3 \times \text{cc. aniline used} \times 100 \times 10}{\text{Weight of Sample}}$$

The aniline content of the reducer sludge can also be determined by acidifying the sample with dilute HCl. The sludge is then transferred to a Gooch crucible and washed thoroughly with boiling water until the aniline hydrochloride is completely washed out. The filtrate after being cooled with chopped ice is titrated with N/2 sodium nitrite solution. A spot test on starch-iodide paper indicates the end point.

Determination of Nitrobenzene in Aniline

This method, devised for the detection of very small amounts of nitrobenzene in aniline, has been found to give practically quantitative results when the nitrobenzene is present in amounts less than 0.5 percent. The method may be used to detect .02 percent of nitrobenzene. The time required is approximately three-quarters of an hour.

The method depends upon distillation with steam of the nitrobenzene present from a strongly acid solution of the ani-

line; reduction of the distilled nitrobenzene and titration of the aniline thus formed with N/10 potassium bromate solution.

1. *Reagents:* N/10 bromate solution is prepared by dissolving 3 g. potassium bromate per liter of distilled water. This solution is standardized against aniline according to the procedure given for the standardization of the $KBrO_3$ solution used in the determination of total aniline described below.

Zinc powder C.P.—It should pass through a 100-mesh sieve; 5 g. when carefully shaken with a mixture of 35 cc. conc. HCl (free from iron) and 100 cc. H_2O until all the zinc has dissolved should consume less than 1.5 cc. of the bromate solution. The actual correction due to bromine consumption of the reagents should be subtracted from titration reading found in the analyses (correction *A*).

2. *Procedure:* Make a preliminary rough qualitative test by noting the color of the froth produced by shaking 15 cc. of sample in a test tube with 5 cc. of water. If the froth has a distinct yellow tinge nitrobenzene in amounts exceeding 0.2 percent is probably present. If the froth test is positive take only 25 cc. for analysis. If negative, 50 cc. should be taken. The weight of 50 cc. can be regarded as 51 g.

Transfer the sample to a 1-liter long-necked flask. Add very slowly a volume of conc. HCl four times that of the sample, cooling the flask under running tap water during the addition. The addition should require at least 5 minutes. Connect the flask with a condenser by means of a Kjeldahl connecting bulb. Distill with steam at such a uniform rate that in 20 minutes approximately 125 cc. of distillate are collected in a 500 cc. Erlenmeyer flask which is provided with a glass stopper. In order to test whether the distillation has been carried on properly, collect an additional 5 cc. of distillate in a test tube and add a few cc. of bromine water. If a precipitate appears in the distillate, aniline has been carried over mechanically due either to the poor connecting bulb or to fast distillation. In this case the experiment must be repeated. Rinse the inside of the condenser with approximately 25 cc. of water and add the washings to the

distillate. Stopper the flask and cool to room temperature. Add 15 cc. of 10 percent KBr and titrate the contents with the bromate solution until a 2-minute end-point is obtained with potassium iodide paper, avoiding the removal of any separated nitrobenzene. This titration should not require over 2 cc. of the solution and is a measure of the aniline that may be carried over by a steam distillation (correction B) ; should be subtracted from the total amount of bromate solution used after reduction. Add 10 cc. of iron-free conc. HCl to the solution and then slowly add 5 g. zinc to relieve the pressure in the flask. To hasten the solution of the zinc the flask can be heated to 60° C. after the reaction has been allowed to continue for five minutes. When the zinc has dissolved and the evolution of hydrogen has ceased, cool the contents of the flask to room temperature with the bromate solution.

Calculation:

$$\text{Percent nitrobenzene} = \frac{\text{cc. } KBrO_3 - (A + B) \times \text{g. aniline/cc.} \times 132}{\text{wt. of sample.}}$$

Determination of Unnitrated Material in Nitrobenzene

Principle of the Method:

The unnitrated material consists chiefly of benzene which has a boiling point of about 80° C. It is determined by a fractional distillation, which gives all material boiling below 85° C.

Status of the Method:

The method gives results which are very satisfactory, having an accuracy of ± 0.5 percent. The determination requires about one and one-half hours for completion.

Apparatus:

The apparatus consists of a 5-liter round-bottom flask fitted with a vertical column, which is in turn connected to a three foot glass condenser at an angle of about 70 degrees to the column. The vertical pipe consists of an iron pipe 4 ft. long and 1 in. in diameter, filled with pebbles. Fitted to this iron

column is a 3 ft. glass condenser. Water at 85° C. flows through the vertical glass condenser, while tap water flows through the other glass condenser. All connections are made with rubber stoppers, care being taken to have tight joints. It was found necessary to secure the connection between the flask and the column with plaster paris.

Procedure:

The vertical column is disconnected at the joint between the glass condenser and the iron column and 1,000 cc. of the sample poured into the flask through the column. All other connections are then made and the flask is heated with a gas burner. Any nitrobenzene being volatilized will be condensed in the condenser supplied with water at 85° C., but the unnitrated material will be carried over and condensed in the last condenser, which is supplied with tap water. This condensed material is caught in a graduated cylinder resting in an ice bath. The volume of unnitrated material distilled over is determined by a reading of the volume of material (other than water) in the graduate.

Calculations:

Percent unnitrated material =

$$\frac{\text{cc. distillate} \times \text{sp. gr. of distillate}}{\text{cc. sample} \times \text{sp. gr. of sample}} \times 100$$

Note: In the calculation it is satisfactory to use 0.88 as the sp. gr. of the unnitrated material and 1.2 as the sp. gr. of the sample.

The heating of the flask is continued until no further distillate comes over.

Analysis of Nitrobenzene

Determination of Dinitrobenzene:

Mononitrobenzene can be removed from dinitrobenzene by the use of several steam distillations in alkaline solution, the mononitrobenzene being very volatile with steam, while the

dinitro is only slightly volatile. The dinitro benzene remaining behind is determined by the $TiCl_3$ method. To eliminate the interference of any nitrates that may be in the original sample, several water washings are employed to remove these nitrates.

The method gives very accurate results when the dinitro content is less than 5 percent, no higher percentages being investigated. A complete determination requires about three hours for completion, but a number of analyses can be carried out at the same time.

The apparatus and reagents required by this method should be found in any industrial laboratory, except the $TiCl_3$ solution.

Procedure:

About 100 cc. of the sample are well washed in a separatory funnel with water to remove any nitrates or acid which may be present. About two washings are necessary to ensure proper preparation of the sample. In case the sample is acid, it should be neutralized before the water washing.

About 10 cc. of this washed sample is weighed and introduced into a 500 cc. round-bottom flask, 40 cc. of 2 percent NaOH solution are added and the flask connected to a condenser and supply of steam. The condenser is connected through a spray trap to prevent any dinitrobenzene being carried over mechanically. The steam supply is usually a heated two-liter round-bottom flask fitted with a long glass tube open to the atmosphere to act as a safety trap. The mononitrobenzene is now removed by steam distillation as soon as the distillate coming over is clear all of the mononitro has been removed. The residue in the 500 cc. flask is removed to a 1,000 cc. flask and the distillate returned to this original 500 cc. flask and 40 cc. of 2 percent NaOH added. A second steam distillation is carried out as before and the residue added to that in the liter flask. This combined residue now contains all the dinitrobenzene in the original sample. It is made up to 1,000 cc. and 100 cc. aliquot portions used for the $TiCl_3$ titration, which is carried out as described under this determination in the general section.

Calculations:

Percent dinitrobenzene =

$$\frac{10 \times \text{gms. DNB from } TiCl_3 \text{ titration}}{\text{weight of sample}} \times 100$$

Determination of Aniline in Aqueous Solutions *

A simple colorimetric routine method for determining small quantities of aniline in water-still residues is based on the formation of Runges violet. 5 cc. of the dilute liquid is treated with one drop of dilute sodium hydroxide solution, three drops of saturated aqueous solution of phenol, and 4 cc. of a fresh saturated filtered solution of bleaching powder. After standing for one-half hour the liquid is diluted with 50 cc. of water and its color compared with those produced under similar conditions containing respectively 0.10, 0.15, 0.20, etc., percent of aniline.

As the coloration is not permanent a set of standards is prepared by mixing solutions of red and blue inks in suitable proportions, and adding sufficient finely powdered chalk to produce after shaking the degree of opacity shown by actual test liquids.

Testing Diphenylamine for Aniline

A solution in concentrated sulphuric acid becomes at first red and then blue, by the addition of a small particle of potassium bichromate.

Potassium bichromate produces in an acid solution of aniline sulfate a dark green precipitate which becomes violet (aniline black) by a further addition of the reagent. On heating the mixture p. benzoquinone (melt. point 127° C.) distills over.

* W. G. O. Christiansen, J. I. C., 1919, 11, 763.

Vapor Pressure (Tensions of Aniline and Nitrobenzene)

(Neubeck)

Pressure	Aniline	Nitro Benzol
760 mm.	183.9° C.	208.3° C.
700	180.8	205.0
650	178.0	202.0
600	175.0	199.5
550	171.9	196.0
500	168.7	192.5
450	165.8	189.0
400	161.6	184.5
350	156.9	180.6
300	151.5	174.5
250	145.6	168.0
200	138.7	160.5
150	130.8	152.0
100	119.4	139.9
75	111.9	130.1
50	101.9	120.2
45	99.5	117.6
40	96.9	114.9
35	94.0	111.8
30	90.9	108.2
25	87.2	103.9
20	82.8	99.1
15	77.2	93.1

Specific Heat of Aniline

Temperature	Specific Heat	Authority
8–82° C.	.5120	Schiff
12–138	.5231	Schiff
20–25° C.	.5180	Nadejdine

Specific Heat of Nitrobenzene

Temperature	Specific Heat	Authority
5–10°	.3524	Regnault
10–15°	.3478	Regnault
15–20°	.3399	Regnault

Specific Heat of Benzene

Temperature		
21–71°	.4360	— — —

Energy of Gaseity—Latent Heat of Vaporization of Aniline

	Latent Heat Calories per Gramme	Mol
Petit	93.3	8,592.93
Marshal	113.9	10,490.19

Energy of Gaseity Meg-Ergs Per

	Gramme	Mol
Petit	3,941.03	362 969
Marshal	4,811.19	443.110

Flash Point and Ignition Temperature

Flash point, 76° C. Van Schwartz

Heat of Combustion

Aniline

g Kal Per Gram	Kg Kal per Molecule		Observer
	Const Vol	Const Press	
8732	812.6	813.5	St. Kl.
8794	818.5	819.2	Petit
8710	810 6	811.4	St. Haw
8759	815.2	815.9	Lem.
8774	816.6	817.3	Swa.

Solubility of Aniline in Water *

SYNTHETIC METHOD

Temp	Grams of $C_6H_5NH_2$ per 100 grams Aq Layer	Aniline Layer
13.8° C.	3.611	5.12
30	3.7	5.4
50	4.2	6.4
70	5.0	7.7
90	6.4	9 9
110	8.0	13.0
120	9.1	14.6
130	11.2	16.9
140	13.5	19.5
150	17.1	24
160	22.0	32
165	26.1	

The critical solution temperature for aniline and water is 168°.

100 cc. H_2O dissolves 3.481 aniline at 22°.

Vol. of solution 103.48

Specific gravity 0.9986

100 cc. aniline dissolves 5.22 cc. water at 23°.

Vol. of solution 104.96

Specific gravity (Herz, 1898) 1.0175

* According to Sedgwick, Pickford and Wilsden, 1911.

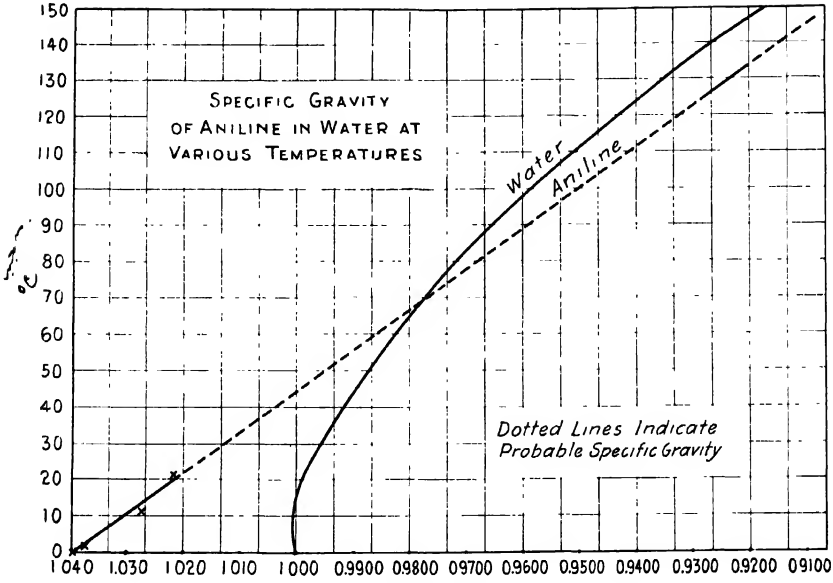


FIG. 20.
Specific Gravity Curves.
Aniline in water.

Solubility of Aniline in Aqueous Salt Solutions at 18° *

Aq. Solution	Gm. Salt Per Liter	(Gms. Aniline) Per 100 Gr Solvent
H_2O Alone	0	3.61
0.5 N KCl	37.3	3.15
1 N KCl	74.6	2.68
1 N NaCl	58.5	2.55
1 N NaOH	40.46	1.90
1 N LiCl	42.48	2.80
1 N $CaCl_2$	67.25	3.00

Solubility of Aniline in Aqueous Aniline Hydrochloride Solutions at 18°

Percent $C_6H_5NH_2HCL$ In Solvent	Grams of $C_6H_5NH_2$ per 100 Grams of Solvent
5 % Soln	3.8
12 % Soln	5.3
30 % Soln	39.2
35 % Soln	50.4

It is evident from the above that aniline is more soluble in aniline hydrochloride than in water.

* Euler, L., Physik Chem., 49, 307, 04.

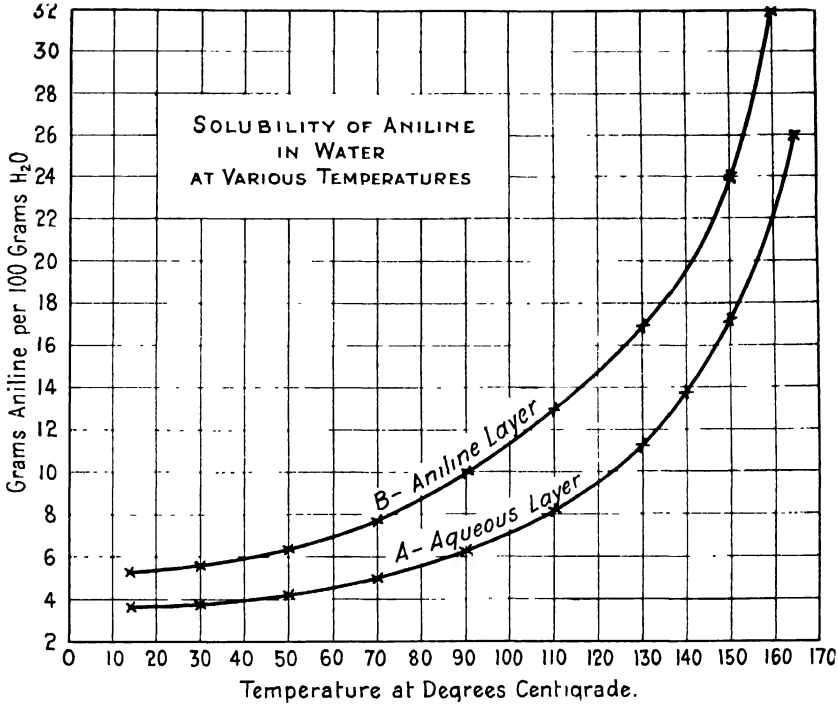


FIG. 20A. Mutual Solubility Curves. Aniline and Water.

Aniline Hydrochloride—Distribution between Water and Aniline at 25° *

100 cc. H_2O dissolves 17.8 grams of salt at 15°.

100 cc. H_2O dissolves 107.1 grams of salt at 25°.

100 grams of saturated solution in water contains 52.1 gms. aniline hydrochloride at 25°.

100 grams of saturated solution in aniline contains 8.89 gms. aniline hydrochloride at 25°.

Caq	Can	Caq/Can	Caq	Can	Caq/Can
0.11	0.006	19.30	0.8	0.47	1.70
0.2	0.020	10	0.9	0.631	1.43
0.3	0.043	6.98	1.0	0.804	1.24
0.4	0.086	4.65	1.1	1.005	1.00
0.5	0.146	3.43	1.2	1.228	0.98
0.6	0.219	2.74	1.3	1.412	0.92
0.7	0.327	2.14			

Caq—grams of salt per 100 grams of aqueous layer.

Can—grams of salt per 100 grams of aniline layer. * Peddle & Turner—1913.

Distribution of Aniline Between Water and Benzene at 25° C.*

Grams $C_6H_5NH_2$ per 100 grams cc.		
Water Layer	Benzene Layer	Ration Ratio
0.0135	0.1312	9.7
0.0122	0.1282	10.5
0.0065	0.0656	10.1

Solubility of Benzene, C_6H_6

SOLUBILITY IN WATER AT 20° (HERZ)

100 cc. water dissolve 0.082 cc. C_6H_6 Vol. of solution 100.082, sp. grav. 0.9979

100 cc. C_6H_6 dissolve 0.211 cc. H_2O Vol. of solution 100.135, sp. grav. 0.8768

Solubility of Water in Benzene (Graschuff)

Temp	Grams H_2O per 100 grams Sat. Soln	Temp.	Grams H_2O per 100 grams Sat. Soln
3	0.030	55	0.184
23	0.061	66	0.255
40	0.111	77	0.337

Mutual Solubility of Nitrobenzene and Water (Davis)

GRAMS NITROBENZENE PER 100 GRAMS

Temperature	Water Layer	N. B. Layer
20° C.	0.19	99.76
40	0.3	99.6
60	0.4	99.3
80	0.8	99
100	1.0	98.7
120	1.3	98.2
140	1.9	97.2
160	2.8	95.8
180	4.2	93.7
200	7.2	91.0
220	11.8	87
230	15.8	83
240	23	72
241	26	67
242	32	58
245.5 Critical Temp.	50.4	

* Farmer & Worth, 1904.

ANILINE DISTILLATION TESTS

Aniline Distillation

ORDINARY DISTILLATION OF 500 CC. ANILINE ADDING 100 CC. WATER FROM TIME TO TIME TO KEEP BOILING POINT OF SOLUTION AT 100° C.

Time	Water Added	Temp of Liquid	Temp. of Vapor	Ratio Water to Aniline	Total cc H_2O Distd Over	Total cc. Aniline Distd Over
32″	100	102.5	99.5	3.7	76.5	20.5
1′ 0″	200	100.7	99	3.7	161.5	43.5
1′ 20″	300	100.5	99.2	4.1	256.5	66.5
2′ 0″	400	100.2	99	3.6	357.5	94.5
2′ 32″	500	100.5	99	4.0	452.5	118.5
2′ 58″	600	100.5	99	3.9	546.5	142.5
3′ 16″	700	100.7	99	4.6	656.5	166.5
3′ 41″	800	100.6	99	3.8	750.5	191.5
4′ 7″	900	100.6	99	3.8	850.5	217.5
4′ 32″	1,000	100.7	99	4.0	950.5	242.5
5′ 1″	1,100	100.7	99	3.8	1,060.5	271.5
5′ 24″	1,200	100.7	99	4.0	1,149.5	293.5
5′ 57″	1,300	100.5	99	3.8	1,252.5	320.5
6′ 21″	1,400	100.7	99	4.2	1,350.5	344.0
6′ 51″	1,500	100.5	99	3.9	1,446	368.5
7′ 25″	1,600	100.8	99	4.1	1,549	393.5
7′ 42″	1,700	100.8	99	4.1	1,647	417.5
8′ 4″	1,800	100.7	99	4.1	1,749	442.5
8′ 26″	1,900	101	99	4.3	1,851	466.5
8′ 45″	2,000	100.8	99.2	4.2	1,951	490.5
9′ 1″	2,100	100.8	99.5	5.5	2,035	505.5

Aniline Distillation Tests

ORDINARY DISTILLATION OF EQUAL VOLUMES OF ANILINES AND WATER USING EXTERNAL HEAT

Time	Temp of Liquid	Temp of Vapor	Ratio Aniline H_2O	Total cc H_2O Distilled Over	Total cc Aniline Distilled Over
0″	100° C.	99° C			
15″	100	99	4.6	37	8
30″	100	99	4.5	73	16
45″	100.5	99.5	4.1	106	24
1′ 0″	100	99	4.3	138.5	31.5
15″	100.5	99.3	4.6	170.0	39.2
30″	100.3	99.3	4.6	228.8	51.2
45″	100.3	99.3	4.7	187.3	63.7
2′ 0″	100.4	99.3	4.8	345.3	75.7
15″	100.5	99.5	4.7	406.0	88.7
30″	102.0	99.8	4.6	459.5	100.2
38″	130	104	4.2	482.5	105.8
					Water layer disappeared
45″	140	108.0	3.8	492.0	108.7
3′ 0″	184	182.5	0.13	496.0	140.7
3′ 15″	184	182.3	0	496+	180.7
					Removal of H_2O complete
			Unacctd. for 4−		
Total				500	500

Aniline Distillation Tests

INCREASING CONCENTRATION FOR EQUAL VOLUMES

Jacket Distillations

Cc. aniline	15	30	45
Cc. water	345	330	315
Percent aniline	4.2	8.3	12.5
Temp. when oil rises (very approx.)	61° C	67° C	70° C
Temp. when solution clears up	101.0	101	101
Temp. when oil is all out	101.3	101	102
Aver. temp. of distillation	101.1	101	101.5
Ratio of H_2O : aniline in dist. when soln. clears	No. dist.	No. dist.	4.7 : 1
Amt. of distillate when soln. clears up	171 cc.	30 oil, 141 H_2O	
Ratio of H_2O : aniline to get aniline from soln.	9.1 : 1	5.7 : 1	6 : 1
Ratio of H_2O : aniline to remove all aniline	9.1 : 1	5.7 : 1	5.1 : 1
No. of cc. H_2O to carry over aniline	136.5 cc.	172 cc.	232 cc.

Aniline Distillation Tests

VACUUM DISTILLATION OF EQUAL VOLUME OF ANILINE AND WATER

300 cc. water, 300 cc. aniline used

Time	Temp. of Liquid	Ratio H_2O to Aniline	Total cc H_2O Distilled Over	Total cc Aniline Distilled Over
15″	26° C.	18.3	55	3
30″	36° C.	10.6	150	12
45″	38° C.	11.1	228	19
1′ 0″	98° C.	0.6	265	82
1′ 15″	98° C.		265	190
Total			300	300

Distillation of Aniline Water Containing Small Amounts of Aniline

	Run No					
	1	2	3	4	5	6
Started distillation — Aniline	10	15	10	30	15	45
Started distillation — Water	300	345	200	330	150	315
% aniline in water	3.2	4.2	4.3	8.3	9.1	12.5
Average temp. of distillation (uncorrected)	101	101	101	101	101	101
Ratio water to aniline to get out aniline not in solution					4.9 : 1	4.7 : 1
Ratio water to aniline to get out aniline in solution	10 : 1	9.1 : 1	9 : 1	5.7 : 1	8.3 : 1	6 : 1
Ratio water to aniline to remove total aniline	10 : 1	9.1 : 1	9 : 1	5.7 : 1	6.4 : 1	5.2 : 1

Aniline Distillation Tests

STEAM DISTILLATION OF ANILINE STARTING WITH PURE ANILINE

Time	Temp. of Liquid	Temp. of Vapor	Ratio of H_2O to Aniline Distilling Over	Total cc. H_2O Distilled Over	Total cc. Aniline Distilled Over
0″	102	99			
15″	101	100	4.0	46.5	11.5
30″	100	99	4.5	87.5	20.5
45″	100	99	6.7	154.5	30.5
1′ 0″	100.5	99.5	4.6	205.5	41.5
15″	101	99	4.6	157.5	52.5
30″	100.5	99.5	4.7	307.7	63.3
45″	100.5	99.5	5.5	379.7	76.3
2′ 0″	100.5	99.5	5.1	450.7	90.3
15″	101.0	99.5	4.8	512.7	103.8
30″	101.0	99.5	4.5	557.7	113.8
45″	101.0	99.5	5.0	632.7	120.8
3′ 0″	100	99.5	4.9	700.7	142.8
15″	100	99.5	4.9	769.7	156.0
30″	100	99.6	5.3	848.7	171.8
45″	100	99.6	5.2	932.7	187.8
4′ 0″	100.3	99.7	4.7	998.7	201.8
15″	100	99.5	4.8	1,056.7	213.8
30″	100	99.5	5.6	1,141.7	228.8
45″	100	99.5	5.4	1,211.7	241.8
5′ 0″	100	99.5	5.6	1,301.7	257.8
15″	100	99.5	5.4	1,382.7	272.8
30″	100	99.5	5.3	1,456.7	286.8
45″	100	99.3	5.5	1,538.7	301.8
6′ 0″	99.7	99.6	5.5	1,616.7	314.8
15″	100.3	99.4	4.8	1,668.7	326.8
30″	100	99.5	5.3	1,737.7	339.8
45″	100.2	99.5	5.7	1,806.7	351.8
7′ 0″	100.2	99.5	5.5	1,872.7	364.8
15″	100.3	99.5	5.4	1,948.7	378.8
30″	100	99.5	5.7	2,034.7	393.8
45″	100	99.5	5.5	2,105.7	406.8
8′ 0″	100	99.5	5.7	2,173.7	418.8
15″	100.3	99.6	6.0	2,299.7	439.8
30″	100.7	100	11.1	2,421.9	450.8
45″	100.5	100	51.0	2,523	451.8
9′ 0″	100	100	No aniline		
				Unaccounted for 47.2	
Total				2,523	500.0

Various Types of Steam Distillation of Aniline

Run 1.—Distillation of Equal Amounts of Aniline and Water in Vacuo.
Run 2.—Distillation of Equal Amounts of Aniline and Water, Atmospheric Pressure.
Run 3.—Steam Distillation.
Run 4.—Distillation of Aniline adding Water in small Increments.

	Run No			
	1	2	3	4
Started with { g. aniline	500*	500	500	500
Started with { g. water	500	500		100
Stage I. *Aniline Water Distillation*				
g. aniline distg. over	31	100	480	485
g. water distg. over	380	460	2,300	1,951
% aniline distg. over	6.3	20	92	97
% water distg. over	76.0	96.4	—	—
Ratio of water to aniline	12 : 1	4.6 : 1	5.1 : 1	4.7 : 1
Temp. of vapor in 0° C.	37.0	99.3	99.5	99.0
Time of distn. hr.-mins.	1′ 15″	2′ 30″	8′ 0″	8′ 45″
Stage II. *Transition Period*				
g. aniline distg. over	105.0	80	20	15
g. water distg. over	61	40	350	84
% aniline distg. over	21.0	16.0	8.0	3.0
% water distg. over	-	3.6	—	—
Ratio of water to aniline	1 : 1.7	1 : 2	16 : 1	5.6 : 1
Temp. of vapor in 0° C. (uncor.)	98	99.3–182.3	100	99.5
Time of distillation	0′ 25″	0′ 15″	0′ 45″	0′ 15″
Stage III. *Final Period*				
g. aniline distg. over	364	320	0	0
g. water distg. over	0	0	Inf.	Inf.
% aniline distg. over	72.7	64.0	0	0
% water distg. over	0	0	Inf.	Inf.
Temp. of vapor in 0° C. (uncor.)	98° C.	182.3	100	100
Time of distillation	30″	45″	Inf.	Inf.
Total time of distillation	2′ 10″	4′ 0″	8′ 45″	9′ 0″

* 300 g. actually used but figures were calculated to a basis of 500 g. for use in this table.

CHAPTER XIII

VARIOUS METHODS FOR PREPARING ANILINE OIL

Catalytic Process of Badische Aniline and Soda Fabrick, U. S. Patent 1,207,802

This process claims to be an improvement over the continuous catalytic method previously patented by Senderens (German Pat. 139,457), by which aromatic amines are produced by passing the vapors of nitro compounds at elevated temperatures (300° C.) together with hydrogen over a suitable catalytic agent. The latter patent mentions copper, nickel, cobalt, iron and platinum as catalysts, the first in the form of copper shavings or dust being preferred. The temperatures used were between 300°–400° C., such temperatures according to the patent claims of "Badische" being entirely too high, thus breaking up the aromatic amines and resulting in low yields which finally was responsible for the patent being permitted to lapse.

If, however, it is claimed catalytic agents containing copper prepared pyrogenetically from one of its salts along with a body promoting the action of the said copper is used, the manufacture, of aromatic amines becomes simpler. Better yields are obtained and the process can be carried on continuously at lower temperatures by using carbon monoxide, hydrogen or a mixture (water gas) as the vehicle for intorducing the nitro body.

Example I.—Prepare a paste of 130 parts of pumice and a mixture of 20 parts of a 40 percent silicate of soda solution, 24.3 parts copper carbonate, 2.7 parts zinc carbonate and a little water. Place the mass into a furnace and reduce it with hydrogen at a temperature from 180°-200° C. and then pass over this catalytic agent a mixture of nitrobenzene vapor with an excess of hydrogen maintaining an internal temperature of 200° C. The gases leaving the furnace are copled and condensed. A mixture of aniline and water is obtained from which the aniline can be separated and obtained practically pure with a fairly high yield. The catalyst retains its activity for a long period.

Example II.—Prepare catalyst by mixing 130 parts of pumice, 124 parts of a mixture containing 90 percent of copper carbonate and 10 percent zinc carbonate, 20 parts of a 40 percent solution of silicate of soda along with a little water. The mass is dried and reduced at 200° C. in a furnace by means of purified water gas. Now with the temperature controlled at 190°–200°, a current of nitrobenzene vapors along with purified water gas is delivered to the furnace. On cooling the gases which leave the furnace a mixture of aniline and water is obtained.

Process of Dr. Conway—German Patent 281,100

Reduction of Nitrobenzene Using Iron as a Catalyst under High Temperatures and Pressures

Aniline can be made by the reduction of nitrobenzene with hydrogen or gas mixtures containing hydrogen in the presence of a catalyst and water, using high temperatures and pressures. It is recommended that the thinning of hydrogen with carbon dioxide be resorted to, due to the possibility of violent reactions at high temperatures and the explosive nature of the decomposition products.

Thirty parts of nitrobenzene and 4 parts of water are charged into an autoclave with some iron borings. The machine is closed and 30 atmospheres of carbon dioxide and 60 atmospheres of hydrogen are delivered under pressure. The total pressure at the start is thus 90 atmospheres (over 1,300 lbs. per sq. inch). When the temperature is raised to 300°–350° C., a rapid absorption of hydrogen takes place, as a result of which the pressure drops to 130 atmospheres at the constant temperature. When the manometer indicates complete absorption of hydrogen the reduction is complete. The charge can be distilled out of the autoclave under its own heat. The iron borings have not been acted upon to any appreciable degree and can be again used.

Process of Kunz—German Patent 144,809

REDUCTION OF NITROBENZENE TO ANILINE USING SODIUM DISULPHIDE

It has been found that sodium disulphide acts as a good reducing agent for converting nitrobenzene to aniline by simple boiling. The action is represented as

$$C_6H_5NO_2 + H_2O + Na_2S_2 = C_6H_5NH_2 + Na_2S_2O_3.$$

The resulting sodium thiosulphate is recovered later by simply evaporating and crystalizing from its mother liquor.

Process of Aktiengesellschaft fur Aniline Fabrikation—German Patent 204,951

INTERACTION OF CHLOROBENZENE AND AMMONIA

If a mixture of 200 parts of monochlorobenzene with strong aqua ammonia 26° (600 parts) is heated in an autoclave for 24 hours at 180° C., aniline is formed. Copper sulphate (25 parts) is added to accelerate the reaction. The reaction mass is delivered to a kettle in which it is acidified with sulphuric acid, the aniline sulphate being subsequently filtered off. The base is obtained as usual by neutralization and steam distillation. The yield is claimed to be about 80 percent of theoretical.

Method of Brochet—English Patent 22,523

USE OF HYDROGEN WITH NICKEL CATALYST

When hydrogen is caused to react in the presence of a nickel catalyst upon nitrobenzene, aniline is obtained directly without any intermediate products. If such reaction takes place in alkaline caustic solution intermediate products azoxy, azoic, hydrozoic derivatives are obtained in succession. These derivatives may be directly converted to aniline by treatment with hydrogen in neutral solution. Thus 0.5 to 5 percent of caustic soda and 10 percent of reduced nickel are added to the nitrobenzene and the whole subjected to the action of hydrogen under a pressure of 10–15 kilos per sq. cm. at 100°–120° C. In this

manner azoxy-benzene is formed and separated from the excess nitrobenzene, and the small amount of aniline formed is steam distilled. The azoxy-benzene is dissolved in amylalcohol to which 10 percent reduced nickel has been added. The charge is subjected to a pressure of 10–15 kilos per sq. cm. at 100° C. The conversion to aniline is rapid, the hydrogen absorbed to effect the conversion of the azoxy being practically theoretical.

Hochst Process—German Patent 282,492

USE OF HYDROGEN WITH A NICKEL CATALYST

In recent years the manufacture of aniline by the reduction of nitrobenzene in the presence of finely ground iron and ferrous chloride has found a strong competitor in the continuous method of production using hydrogen and a nickel catalyzer. This method is based on the process of Farbwerke vorm. Meister Lucius & Bruning, a digest of which is herewith given.

"It has been found that aromatic nitro-compounds which are volatile with steam can be easily reduced by distilling such amines with steam in the presence of hydrogen gas over any catalyst suitable for hydrogenation. These reductions take place consequently at temperatures below the boiling point of the nitro-compounds. The resulting reduction products are colorless and free from tarry decomposition products. The catalyst is used in the form of a fine powder as such or is precipitated over an inert substratum. Steam saturated with the nitro-compound, and mixed with hydrogen gas is passed over the catalyzer, the reduction compounds along with water being then condensed and run into a reservoir, the excess of hydrogen passes through the condenser to a reservoir from which it is again introduced into the system.

"Most of the processes previously published, pertaining to the reduction of volatilized nitro-compounds with hydrogen in the presence of a catalyst, recommend heating the catalyzer to a temperature higher than the boiling point of the nitro-compound under consideration. At such temperatures (for example at least 200° C. for nitrobenzene) the nitro- and the resulting amino-

compounds are partially decomposed, and an overreduction takes place which may consist of splitting off the amino group and the addition of hydrogen. (Hydrogenation of the benzene ring.)

"On the other hand, if the catalyzer is used at a temperature below the boiling point of the nitro-compound, in order to keep the reduction temperature down, some of the nitro-compound is condensed on the catalyzer which is consequently weakened. This is the condition which prevails in the employment of British Patent 2,520/1907, which recommends spraying of the nitro-compound on the catalyzer. The use of reduced pressures in conjunction with the spray system is also found unnecessary, British Patent 9,112/1908, as making the system unduly complicated.

"Thus by volatilizing the nitro-compounds with steam in the presence of hydrogen and a catalyzer working at lower temperatures is made practicable. The catalyzer is heated to the same temperature as the gases passing through. The process is in the nature of a purification of the nitro-compound by steam distillation and is in fact a continuous reduction operation.

"The reduction apparatus is a horizontal tube half filled with nickel powder. This is heated by means of a jacket to 120° C. to prevent condensation of the steam. At the beginning of the operation unit there is a tank of nitrobenzene which is heated by means of a jacket or coils to 120° C. High pressure or superheated steam along with hydrogen are bubbled through the nitrobenzene reservoir at the above temperature. An excess over the theoretical amount of hydrogen must be metered out, to which is added the constant surplus recovered from the end of the system. The rate of the steam-gas-vapor mixture is regulated so that the aniline at the exit of the condenser system is absolutely free of nitrobenzene."

The aniline is rectified as usual after separation from the accompanying water. The aniline water can be worked up either in stills for that purpose or preferably in an aniline boiler to supply the steam for the operation. The yield is 73.0 or about 1½ points better than that obtained by standard operation by

the use of iron and hydrochloric acid. This is due to the simplicity of the system.

In actual operation the system is warmed up to the proper temperature before starting. The first runnings from the condenser (until the flow rates are adjusted) are tested for the presence of nitrobenzene, this distillate being led to a separate tank to be combined with fresh nitrobenzene later on. When the product is clear, and the valves all set, the operation becomes quite simple, slight adjustments being made when alternate tanks of nitrobenzene are brought into use.

Six parts of steam are required to volatilize one part of nitrobenzene. The water thus obtained from the use of steam as a vehicle for carrying the nitrobody, after separating the free aniline oil for rectification, must be regenerated as steam in a special aniline boiler, in order that this process can compare favorably with processes previously outlined.

An analysis of the reduction formula shows that at least six molecules of hydrogen will have to be supplied for the reduction of each molecule of nitrobenzene volatilized.

$$C_6H_5NO_2 + 6H \rightarrow C_6H_5NH_2 + 2H_2O.$$

The hydrogen for the operation may be produced by electrolysis but it is possible to utilize the method of the Badische Aniline and Soda Fabrik, in which hydrogen is generated along with carbon monoxide by passing steam over heated coke. This blue water gas is an excellent inexpensive reduction medium which is used (according to patent claims) by the above company along with its own catalytic method for the production of aniline. However, pure hydrogen is preferably used, and may be obtained from the blue water gas by passing alternating blasts of steam and gas over iron oxide. The monoxide is oxidized to CO_2, which is absorbed in alkaline solution. The pure hydrogen is collected in a gasometer.

The productivity of a unit reducing 500 lbs. per hour or 12,000 lbs. per day is equivalent to the total production obtained daily from three 1,600 gal. reduction machines. The prime cost of the product will be slightly lower due to the increased yields obtained

by this continuous process. The costs of raw materials will be practically identical as the burden due to the production of hydrogen and the maintenance of an efficient catalyzer unit is about the same as charged against the introduction of iron borings and acid for the reduction process. The power charges for the continuous process are about the same for both methods as the greater steam and water consumption in the continuous process is counterbalanced by the practical elimination of the electric current required for driving the reducers and accessory equipment.

Blue water gas as produced at a large American plant has the following composition after scrubbing the solid particles but before passing through solutions for the removal of carbon dioxide.

Hydrogen	50%
Carbon monoxide	43%
Nitrogen	3%
Carbon dioxide	3%
Methane	1%
	100%

The cost per 1,000 cubic feet of this gas when produced at the rate of 1,500,000 cu. ft. daily is less than fifty cents. If 42 lbs. is taken as the estimated weight per 1,000 cu. ft. of blue water gas it is evident that the net cost of the combined carbon monoxide and hydrogen will be over one cent per pound. If, however, only hydrogen is utilized the cost per pound of this gas for reduction would be about thirty cents, as is evident from the following composition diagram:

$$1 \text{ cent per pound} < \begin{array}{l} CO = \text{mol. weight } 28 \\ H = \text{“} \quad \text{“} \quad 1 \end{array}$$

It is doubtful if any of the preceding processes can hope to compete with the standard method of reduction with finely divided iron borings using ferrous chloride as a catalyst. Only the process of Farbwerke Meister Lucius Bruning using a mixture of steam and hydrogen as a vehicle for carrying vaporized nitrobenzene can be considered as a formidable competitor.

CHAPTER XIV

THE DERIVATIVES OF ANILINE

The manufacture of aniline on a commercial scale gave the first impetus to the development of the color industry. At first aniline was used almost exclusively as the starting point in the production of synthetic dyestuffs and consequently the term "Aniline Dyes" came to be used as a popular expression to cover practically all coal tar intermediates and dyes. It is noteworthy that now only a small proportion of the total dyes produced are actually derived from aniline.

From the position of an importing country in 1914, the industry in the United States has developed to gigantic proportions. According to data obtained from "Census of Dyes and Coal Tar Chemicals" * compiled by the U. S. Tariff Commission, the production of nitrobenzene and aniline for the past few years has been as follows:

Production of Nitrobenzene

Year	Lbs Made	Price
1918	38,250,332	15.0 cents
1919	12,544,017	13.9 cents
1920	53,244,008	14.0 cents
1921	7,443,192	12.0 cents
1922	37,833,561	9.0 cents
Total	179,315,110	
Annual Average	35,863,022	

Production of Aniline

1918	24,102,129	27.0 cents
1919	24,345,786	24.4 cents
1920	39,234,186	28.0 cents
1921	5,639,234	22.0 cents
1922	21,401,864	15.0 cents
Total	114,723,199	
Annual Average	22,944,640	

* Data from this publication used throughout chapter.

Aniline Consumption

In response to an inquiry sent to aniline manufacturers of the country, the following general sources of consumption were reported:

	Figures from complete Dye Plants	Figures from small Aniline Plants
Used for Dye Intermediates	50%	35%
Textile Trade	10%	25%
Rubber Business	25%	30%
Paint Manufacture	10%	5%
Other purposes	5%	5%

Based on the figures reported by the U. S. Tariff Commission in the "Census of Dyes of Coal Tar Products," the average annual production of 23,330,000 lbs. may be roughly distributed as follows:

	Textile Trade	3,000,000 lbs.
	Rubber Business	6,000,000
Directly in Finished Dyes	Indigo	5,000,000
	Direct Black E.W.	1,000,000
Intermediates	Dimethylaniline	2,800,000
	Diethylaniline	50,000
	Paranitroaniline	1,350,000
	Diphenylamine	1,250,000
	Sulphanilic acid	900,000
	Aminoazobenzene	90,000
	General	1,560,000
	Total	23,000,000 lbs.

Aniline finds, as can be seen from the preceding table, its greatest uses in the manufacture of aniline salt for direct production of aniline black on the fibre, sulphanilic acid, acetanilid and paranitroaniline, diphenylamine, dimethylaniline, diethylaniline, aminoazobenzene, ethylbenzylaniline, direct deep black E.W. and in the production of indigo from phenylglycine. To this is added the consumption of aniline for various intermediates used in the rubber industry as accelerators, and finally a host of derivatives not finding so wide a commercial application at present. Only the more important of these derivatives are considered here.

An effort is made, however, not only to give a practical tested outline of manufacture, but also to designate its commercial importance and fields of application.

Derivatives of Aniline with Acids

ANILINE HYDROCHLORIDE

$$H_2N \cdot HCl$$

Production:

Year	Lbs. Made	Price
1918	1,765,359	34.0 cents
1919	1,446,909	24.8 cents
1920	2,024,956	37.0 cents
1921	366,533	27.0 cents
1922	825,558	22.0 cents
Total	6,429,317	
Average annually	1,285,862	

Aniline used—approximately—1,000,000 lbs.

Description of Operation:

To obtain very pure white aniline salt the following process is used. Calculated quantities of water-white aniline and pure hydrochloric, free from iron, are mixed with a small amount of clear water in an agitated chemical-ware vat. The aniline is fed under the surface of the diluted acid and the mixture agitated until the feeding is complete. The charge is then drawn into an enamel-lined, jacketed, vacuum graining kettle. After the charge is in the kettle, the jacket is steam heated and the solution evaporated to dryness in vacuo. The product is practically pure and the yields are quantitative. Care should be taken in preparing the solution, in order to avoid excess acidity.

The more customary method of manufacturing as followed out by producers of aniline is to mix calculated amounts of aniline and pure hydrochloric acid in earthenware or lead-lined vessels. The mixture is run into either a lead trough or earthenware crocks around which cooling water is circulated. Upon cooling, the grey crystals of aniline hydrochloride separate out.

These crystals are removed and delivered to a centrifuge, the basket of which is lead lined or made of hard rubber.

The mother liquor is then drawn from the containers and delivered to the aniline reducers where it replaces hydrochloric

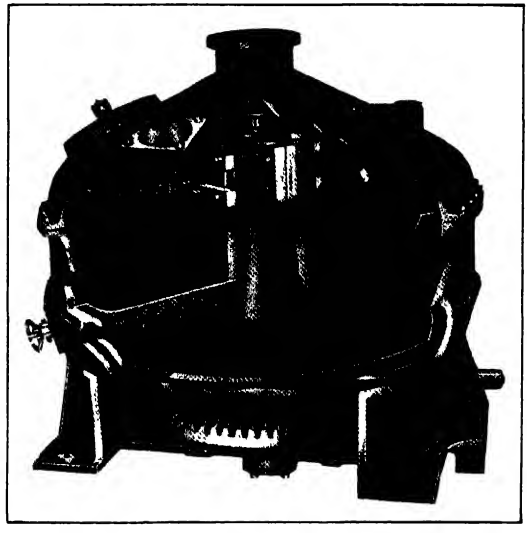


FIG. 21.
Jacketed Crystallizing Kettle.

acid, as the catalyst in the reduction process. The hydrolysis of aniline salt in the presence of finely divided iron to yield aniline and free acid has been previously discussed. (See Chapter II.) Its successful use in the reduction process as noted here is convincing confirmation that the equations suggested are a true interpretation of the reaction.

Aniline hydrochloride forms white crystals melting at 198°. It is readily soluble in water and alcohol.

Uses:

Practically all of it is used for the production of aniline black in the textile industry, or in the fur dyeing industry, a small quantity only going for the production of magenta, nigrosin, indulin and other intermediates.

Aniline Black

When aniline is oxidized on the fibre with oxidizing agents it produces a black dye belonging to the class of ingrained colors.

History:

This reaction was first noticed by Runge in 1834 when chromic acid was added to aniline. Wilson, in 1860, described the reaction. In 1863, Lightfoot patented the first successful method of dyeing directly on the fibre using potassium chlorate and cupric chloride as oxidizing agents.

The following oxidizing agents are now successfully used: Chlorates, Chromates, Copper salts, Vanadium salts, Tungsten salts, Cerium salts, etc.

The structure of the final black is very complicated and is still obscure. It has been demonstrated that the oxidation goes through three stages:

1st. To Emeraldine, which is the earliest stage—grayish green in color, 4 or 8 benzene rings being linked by NH groups.

2d. To Nigraniline and Pernigraniline, consisting of 8 benzene rings linked by $-N=$ and

3d. The so-called ungreenable black.

The second stage is affected by weak acids and weak oxidizing agents and easily turns green; the final product is quite stable.

There are three common methods of dyeing:*

Dyed Blacks
Aged Blacks
Steamed Blacks

I. *For Dyed Blacks.*—Aniline hydrochloride is treated with sodium dichromate and H_2SO_4, gradually raising the temperature to the boiling point. The yarn is finally steamed.

II. *For Aged Blacks.*—Cotton saturated with a solution of aniline salt and some oxidizing agent as sodium chlorate and an oxygen carrier as vanadium chloride or sulphate. The yarn

* See Mathews for detailed description of these and other methods for Aniline Black.

is then dried and aged by passing through a moist air chamber at 30°–45° C. This brings color to the nigraniline stage and it is then treated with sodium dichromate solution in order to get ungreenable black.

This method is chiefly used in calico printing. It has the drawback of giving the cotton the tendency to tender unless carefully applied. In this class is included the air oxidation method in which air is used instead of a chlorate. A catalyst or oxygen carrier such as vanadium salts is used. Instead of mineral acid, formic acid is used to reduce the danger of tendering the fibre. Some paraphenylenediamine is added to the aniline to catalyze the oxidation.

III. *Steaming Method for Steam Blacks.*—This process is most costly but is productive of the best results. The cotton is here steamed for a short time after saturating with an oxidizing solution and drying. It is then chromed. Aniline black is not generally used for wool, silk, or animal fibres.

Sulphonation

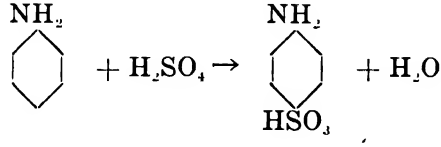
SULFANILIC ACID

Production	Lbs. Made	Price
1918	1,247,478	$0.29
1919	1,023,861	0.24
1920	1,796,838	0.36
1921	1,071,904	0.24
1922	1,515,421	0.19
Total	6,655,502	
Annual Average	1,351,100	

Approximate amount aniline consumed annually, 900,000 lbs.

Process Involved: Sulphonation.

Reaction:



Preparation—Baking Process:

The contents of one drum of aniline (900 lbs.) are emptied into a shallow cast-iron mixing pot or preferably a flat enamel-

lined agitated mixer. 1,050 lbs. of 66° water-white sulphuric acid are then fed in very slowly under constant agitation. A thick paste is obtained and this is removed while warm and placed into shallow tin or iron trays for a vacuum oven. Heat is supplied to the oven by means of superheated steam or a circulating oil system, particularly if one is being used for other work nearby. Some plants heat the oven electrically and are able to obtain a perfect temperature control. The paste is heated at 200° C. for six hours.

The dry cake is emptied from the trays into an iron or preferably a lead-lined mixing kettle, provided with a cover and vent. It is now slightly grey in color and is upwards of 90 percent pure. It contains in this crude form from 0.3 percent to 3.0 percent of unchanged aniline and some carbonaceous impurities. The "bake" is now dissolved in a dilute caustic soda or soda-ash solution until a strong blue coloration with litmus is obtained. This solution is steamed by the injection of steam into it until all traces of free aniline have been removed. It is then run through a small Sweetland filter press to remove the free carbon. The filtrate is now suitable for making azo dyes and in some works is used in this state. The sodium salt is often made by treating the bake first with $Ca(OH)_2$ and then with Na_2CO_3. If a good quality free acid is desired, the filtrate is acidified with sulphuric acid until acid to Congo paper. The sulphanilic acid is then precipitated in a very pure form. The purified material is then put through a filter from which it is removed and dried at low temperatures in a vacuum drying oven.

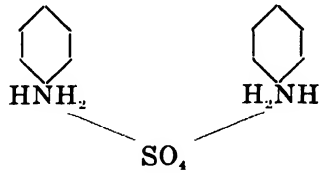
The yield of the pure precipitated acid should be over 150 (based on 100 lbs. aniline used) which is 80 percent of theory.

Sulphonation Process:

Sulphanilic acid can also be made by direct sulphonation, if an excess over the theoretical quantity of sulphuric acid is used. The water molecule is removed from the aniline salt at elevated temperatures by the dehydrating action of the free acid.

Although the reaction is continuous the process may be considered as taking place in two stages:

(1) Formation of aniline sulphate, in which a slight excess over the calculated quantity of H_2SO_4 is used to form the salt of the dibasic acid.



(2) Dehydration stage—in which the excess of sulphuric acid is added at elevated temperatures, and the charge cooked to complete sulphonation.

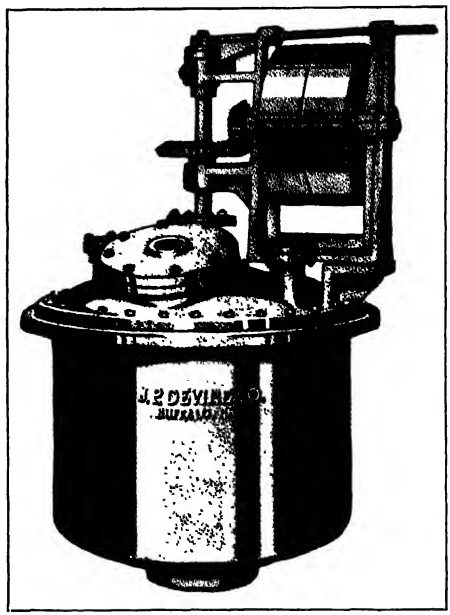


FIG. 22.
Cast-Iron Sulphonator.
(Devine Type.)

The reaction is carried on in a covered, cast iron, sulphonation kettle, which is provided with a sturdy stirrer. The ap-

paratus is set in masonry and arrangement is made for heating by direct fire with a fuel oil burner. A top connection to a vertical reflux condenser is advisable in order to recover any aniline vapors that may escape during the early stages of the reaction.

Formation of Aniline Sulphate:

Theoretical quantities of acid and aniline are brought together to form aniline sulphate. Two hundred twenty-five pounds of 66° sulphuric acid are run into the sulphonator, and then with constant agitation 400 lbs. of aniline are run under the surface of the acid. This feeding operation should consume from one and a half to two hours. The temperature of the charge during the addition should not reach 180° C., in order to avoid loss of aniline. At times it may be necessary to add another portion of acid to the charge in order to keep the charge fluid. At the close of the feeding operation, however, the aniline sulphate should be in solution, with the temperature of the charge about 175° C.

The final addition of dehydrating acid is not started until signs of sulphonation become apparent, as indicated by the appearance of fine crystals of sulphanilic acid in the charge. This does not ordinarily take place until two hours have elapsed from the time of starting. Directly after the aniline feed, a small flame is lighted to heat up the sulphonation kettle. As the temperature rises, more sulphuric acid is added, in periodic shots, to keep the charge fluid. A total of 700 lbs. of 66° acid is used, and the temperature is cautiously brought up from 180° to 215° C., at the rate of about 4° per hour, care being observed to prevent frothing. This latter condition causes carbonization to take place and gives considerable trouble as it is extremely difficult to control after it once makes any headway. The acid is fed in at intervals when it is seen that the sulphanilic acid being formed becomes thick. Too rapid a temperature rise is distinctly conducive to the formation of considerable decomposition products. Towards the close of

the cooking period, samples of the batch are taken and tested for the presence of free aniline.

A small quantity of acid which has been held in reserve is added just prior to discharging, in order to insure a free running charge. The completed batch in the sulphonator is now run into a wooden tub which is prepared with a heel of cold water, the quantity of water being determined by plant conditions. If the sulphanilic acid can be used in suspension in the free acid, considerable water is used. When it is to be prepared for shipment, however, unnecessary dilution is to be avoided, due to the solubility-loss in wash waters. The charge is then pumped on to a filter press and the cake washed with small quantities of cold water to remove most of the free acid and unconverted aniline sulphate. The press-cake is grayish white, and in this paste form contains from 60 percent to 70 percent sulphanilic acid. On a dry basis its purity would be over 99 percent, containing as impurities about 0.25 percent H_2SO_4 and 0.2 percent free aniline. If the control is carefully carried out, no free carbon is present. The yields by this process are approximately 173 lbs. per 100 lbs. aniline used or 691 lbs. for the batch described. This is equivalent to 92–93 percent of theory.

Sulphanilic acid forms two hydrates, the dihydrate obtained by crystallization from its solution below 20° C. is very efflorescent and on exposure to the air soon loses all its water. The monohydrate which separates between 20°–44° retains its water at the ordinary temperature. Sulphanilic acid is soluble in 224 parts of water at 0°, 90 parts at 18.9° and 34 parts at 54.5°.

The acid is used for making Xylene Yellow 3 G, Tartrazine, Helianthine, Orange IV, Azoflavine R.S., Azo Yellow 3 G, Brilliant Yellow S, Chrysoine, Orange 1, Orange 2, AzoFuchsine G, AzoFuchsine 6B, Resorcine Brown, Fast Brown G, Palatine Black A, Anthracene Acid Brown G, Ponceau 10 R.B., Eriochrome Verdone A, Buffalo Black 10 B, Eboli Green, Benzamine Brown 3 G.O., Congo Brown G, Columbia Green, Benzo Brown G, Hessian Brown B.B.N. and Cotton Black.*

* The dyestuffs obtained from the intermediates are throughout this volume

Aniline Condensations

DIPHENYLAMINE

$$\langle\bigcirc\rangle\text{—NH—}\langle\bigcirc\rangle$$

Production annually	960,000 lbs. est.
Aniline used approximately	1,250,000 lbs.

No definite figures regarding production are available. During 1917–1918 the production of diphenylamine was close to 3,000,000 lbs. annually, as its use as a stablizer for explosives made requirements unduly large.

Processes Involved: Condensation.

Reaction:

$$2C_6H_5N\left\langle\begin{matrix}H\\H\end{matrix}\right. + \triangle^* + HCl \rightarrow C_6H_5 - NH - C_6H_5 + NH_3 + HCl$$

Bromine, Iodine, Chlorine, its salts and acids, have all been used and patented as catalysts for this reaction.

Description of Operation:

The manufacture of diphenylamine from aniline is briefly as follows:

Two thousand pounds of aniline containing 30 pounds of 20° Bé. hydrochloric acid are carefully weighed out in the aniline storage house, and then blown to rolled steel autoclaves in the autoclave house. The autoclaves are capped up, and the pressure gradually brought up to about 300 lbs. The charge is cooked for

arranged according to the Schultz number for the dye. The classification according to the usual constitutional headings is therefore as follows:

Nitroso Dyes	Acridine Dyes
Nitro Dyes	Quinoline Dyes
Stilbene Dyes	Thiobenzenenyl Dyes
Pyrazolone Dyes	Indophenol-Oxazine Dyes
Monoazo Dyes	Thiazine Dyes
Diazo Dyes	Azine Dyes
Trisazo Dyes	Sulphur Dyes
Tetrakisazo Dyes	Carbazole Dyes
Auramines-Triphenylmethane Dyes	Anthraquinone and allied dyes
Diphenyl-napthyl-methane Dyes	Indigo Group Dyes
Xanthone Dyes	Aniline Black Group

* The symbol $\triangle$ is used to designate heating at high temperatures.

forty hours, maintaining a pressure of 310 lbs. and a temperature of 290° C. as closely as is possible. The ammonia gas which is formed during the reaction in the autoclave is released every hour, and a temperature and pressure record is kept for every half hour of the run.

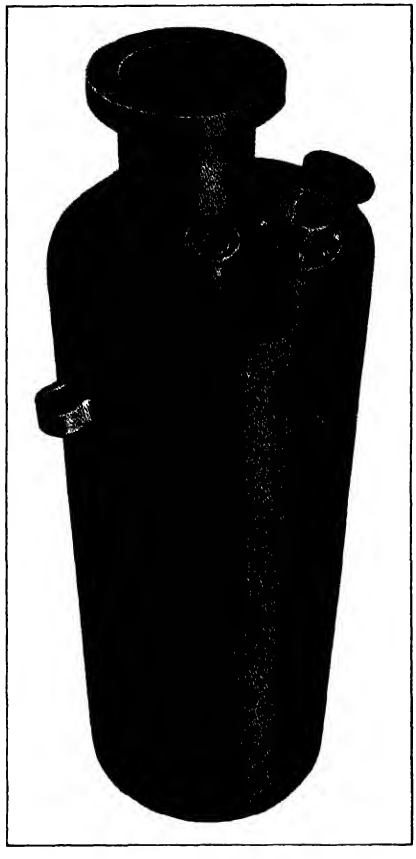


FIG. 23.
Rolled Steel Autoclave.
Hammer Weld. Tested for 1000 lbs. working pressures. (Kellogg Manufacture.)

The reaction may be written as follows:

$$2C_6H_5NH_2 + \Delta + HCl \rightarrow 2C_6H_5NH_2 \cdot HCl$$
$$2C_6H_5NH_2 \cdot HCl + \Delta \rightarrow (C_6H_5)_2NH + NH_4Cl$$
$$NH_4Cl + \Delta \rightarrow NH_3 + HCl$$

The equation shows that 90.9 lbs. of diphenylamine may be realized for every 100 lbs. of aniline actually used.

The ammonia gas is led to the ammonia recovery where it is absorbed. The converted diphenylamine is blown under its own pressure (after cooling to 250 lbs. pressure) to the still house where the unconverted aniline is distilled out and recovered. The residual diphenylamine is fractionated and the comparatively pure material sent to the wash tanks for purification.

The traces of aniline are first washed out with hydrochloric, the soluble aniline hydrochloride going out with the wash waters. The traces of acid are then eliminated by repeated water washings. This crude diphenylamine is then sent to a refining still and the diphenylamine from the distillation is carefully tested as the distillation progresses, and only that fraction which passes specifications is sent to the graining kettles, preparatory to barrelling. The material not passing specifications is run into a rewash tank, and is again washed and refined.

The Recovery of Aniline:

The aniline water and aniline-diphenylamine fractions are both run into a common tank, and later sent for re-distillation, in a separate set of recovery stills. From these aniline stills the aniline water is fractionated, and sent to a storage tank for settling. The aniline fraction is returned to the aniline storage tank to be used again in the autoclaves. The aniline-diphenylamine fraction is sent back to its receiver to be again re-worked, while the diphenylamine fraction is run into the lead tubes for washing. After the aniline water in the storage tanks has thoroughly settled, the aniline is run off to the recovery stills, while the supernatant water is sent to the aniline distillation house to be steam distilled.

About 46 percent of the total aniline autoclaved is recovered by this process. This aniline will contain as high as 4 percent diphenylamine in solution. The color is usually a reddish brown. The aniline fraction is continued until a test with acidulated water shows the presence of diphenylamine.

The Aniline Diphenylamine Fraction is continued until the melting point of the distillate is 50° C. at which time it is turned into the lead wash tanks for purification. At the close of the run the distillate is turned down into the tar tank. These tarry residues are combined, washed, redistilled and then washed again before sending to the refining stills.

The Residue from the autoclave charge is usually a porous carbonaceous mass. However, if the charge were not completely cooked, a thick syrupy mass of tarry diphenylamine would be found present.

Average times for distilling each fraction are:

Aniline water	1 hr.
Aniline diphenylamine	5 hrs.
Diphenylamine	5 hrs.
Tar	1 hr.
Total	12 hrs.

The Purification of Diphenylamine

About 6 to 8 washes are given each charge of about 3,800 lbs. The first wash is a hot water wash, the diphenylamine running into this water. The water is then drawn off through an upper drain valve. The next wash is the acid wash. When the wash water is in the tub and the agitation is on, add sufficient hydrochloric to give a decided reaction with Congo Red paper. For autoclave washes, not over one carboy should be necessary, as a rule one-half of this quantity should be sufficient. From time to time during the washing, the charge is tested with Congo Red paper, to insure an acid reaction at the close of this wash. In case the acidity disappears, more acid is added.

After settling, the acid water is drawn off and the charge washed until neutral. The practice of using soda to insure neutralizing is not found necessary. However, a small amount of soda is added to poor rewash charges at times, as it was found that this material exerted a beneficial effect on the color and melting point of the refined diphenylamine. The average tem-

perature of the wash water is 75° C. Approximately 3 percent of the total diphenylamine made is carried out by wash waters. This diphenylamine is recovered in a system of outside catch boxes. Analysis of wash waters in the catch boxes showed the following results:

Catch Box No. 1, Solid Matter .025 Soln., .007 in suspension.
Catch Box No. 2, Solid Matter .022 Soln., .004 in suspension.
At outlet No. 3, Solid Matter .021 Soln., .004 in suspension.

The total amount of solids lost through this channel should not exceed 1 percent of the yield.

Refining:

After the crude diphenylamine is properly washed it is dropped into a heated blowcase and blown to a refining still. These stills are identical with autoclave stills. A medium fire is applied to insure a uniform rate of distillation. The first part of the run is sent to the rewash tank and only when the melting point is 51.5° C., is the material turned into the graining kettle.

During the diphenylamine distillation, melting point determinations are made every ten or fifteen minutes, so as to insure a satisfactory melting point. Towards the end of the run, the melting point will slowly drop and it is again turned to the rewash tank when it goes below 51.0° C. The graining kettles are cooled by water and when the product feels dry to the hand it is barrelled up.

The Rewash Charge:

The rejected material from the refining stills (along with some of the tar from the autoclave stills if conditions permit) is blown back to the wash house and is again washed. Three washes are given. An acid wash to insure acidity, a soda wash to insure neutrality, then a final clear water wash; the soda treatment supposedly having beneficial effect in getting rid of the tarry bodies. The results of a series of tests covering operating conditions for a long period show that 6 percent loss was

incurred in the autoclave still, and 2 percent was suffered in the refining stills.

Good operating results show a conversion of about 40 and a yield of 78–80 based on aniline actually used.

Another method of purifying the autoclave charges after the reaction is complete is to transfer the autoclave charge to a large vacuum still. Owing to the fact that considerable time is required to effect a distillation several charges are put into the still at one time. An idle still receives fresh autoclave charges so that operations may continue—without interruption —according to a definite schedule.

A slight vacuum may be kept in the still while the charges are being blown into it in order to avoid pressures. Heating of the still may be accomplished by several methods. As soon as the temperature on the still is raised the aniline water fraction comes over and is led to a receiver. The clear aniline fraction is next distilled and this material is sufficiently pure to permit of being used again in the autoclave operation without further treatment. When the aniline is almost all over it becomes contaminated with diphenylamine. The temperature on the still now commences to rise and the water on the still condenser is gradually shut off to prevent the clogging up of the condenser tubes. The aniline-diphenylamine fraction is stored separately and used as a heel for ensuing still charges. When all traces of aniline are absent from samples taken from the distilling line the pure diphenylamine is run into a heated tank preparatory to dropping it into the crystallizing kettles. The tarry fraction at the close of the distillation which does not meet the melting-point specifications can be run into the receiver for the aniline-diphenylamine fraction.

Diphenylamine is also made by the digester process in which a mixture of aniline and aniline hydrochloride is heated.

A low pressure steel autoclave or an enamel-lined digester are charged with equal parts of aniline and aniline salt, 500 lbs. of each. The autoclave is heated up by indirect heat from a fuel oil flame to 260° for 20 hours. A pressure

of 70 to 80 lbs. is realized, and this is maintained by releasing the ammonia every hour. At the close of the autoclaving time the charge may be cooled and later transferred to a tub containing concentrated hydrochloric acid or the entire autoclave batch can after releasing the ammonia be blown under its own pressure into a tub containing water. The aniline hydrochloride and traces of ammonium chloride are thus put into solution and removed while the aniline and diphenylamine are separated by fractional distillation.

By the former method the cooled autoclave charge is treated with 30 percent hydrochloric acid in a wooden tub until it is just acid to Congo. The charge is heated up to 80° and the molten diphenylamine agitated. If it is now cooled the crude diphenylamine is separated out as a solid cake at the base while the mother liquor is run off and the aniline recovered. Its purification from this point is similar to that already described for the catalytic process. The crude base is treated once more with dilute hydrochloric and finally washed with dilute sodium carbonate solution prior to running it out into heated storage tanks.

Its purification can be effected by fractional distillation, distillation in vacuo, or by distilling with superheated steam. For the first method an ordinary still heated in an oil bath or by indirect fire from a fuel oil burner suffices. The second system is more elaborate but is productive of better yields and a purer product. The use of a superheater permits of distilling the charge with steam at 300° C. About one and one-half parts of water are required to distill one part of base. This diphenylamine is obtained as a bright yellow cake if the distillate is run into cold water.

The recovery of the aniline from the mother liquors is a very important part of the operation, otherwise its cost by this method of manufacture would be quite prohibitive.

The conversion by this method is about 50 percent, *i.e.*, 50 lbs. of diphenylamine are obtained from every 100 lbs. of total aniline used. This is slightly better than that obtained by the

catalytic process. The recovery of aniline is about 32 percent of that digested. The yield is thus 73.5 percent of the aniline actually used (86 percent of Theory) which is slightly lower than that obtained by the catalytic method.

Diphenylamine melts at 52 to 54° C. and has a density of 116. It boils at 310° C. It is used for the manufacture of Metanil Yellow, Orange IV, Azoflavine R.S., Azo Yellow 3G, Brilliant Yellow S, Curcumine, and for certain sulphur colors.

DIMETHYLANILINE

$$N(CH_3)_2$$

Production	Lbs Made	Price
1918	4,263,458	$0.57
1919	3,559,654	0.54
1920	5,447,107	0.71
1921	566,286	0.54
1922	2,327,561	0.32
Total	16,164,066	
Average Annually	3,232,813	

Approximate annual aniline consumption: 2,800,000 lbs.

Reaction:

$$C_6H_5NH_2 + 2CH_3OH + (H_2SO_4) \rightarrow C_6H_5NH(CH_3)_2 + H_2O$$

Processes involved—Condensation. Hydrolysis.

Preparation:

The autoclave technique for the manufacture of this intermediate is similar to that of diphenylamine. It is made in large quantities and consequently the autoclave room is fitted up with suitable mechanical devices for removing and replacing the machines, so that they can be periodically inspected and cleaned. The machines are usually set up in a battery with a fire wall separating the autoclave room from the purification room. The autoclaves which are jacketed can be heated individually by means of indirect heat from fuel oil burners or better yet by a central circulating system, which is installed in

a separate shed. Here a high flash oil circulating system is installed. The circulated oil at 250° temp. can then be turned into any autoclave jacket as soon as the machine is ready for heating. The oil piping can be arranged so that the jacket can be drained to effect a more rapid cooling of the charge. The best practice, however, is to use non-jacketed autoclaves and heat by electricity through the medium of resistance coils underneath.

The use of catalyzers to effect the combination of aniline and an alkyl is being developed and its use is becoming more

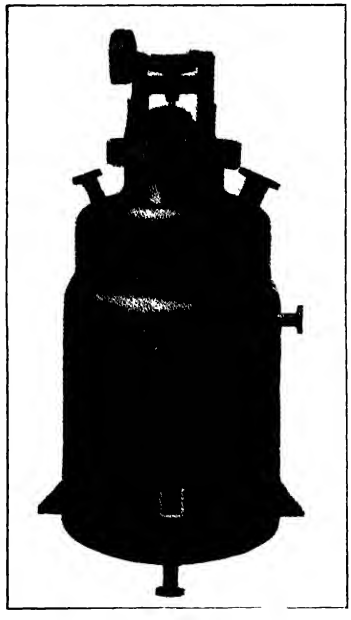


FIG. 23A.
Jacketed Agitated Autoclave.
Made to withstand internal pressures up to 2000 lbs. per square inch.

widespread. In fact this tendency is becoming general for all autoclave reactions.

The methyl alcohol which is used in the reaction (which must be free from acetone and ethyl alcohol to prevent very high pressures) is acidulated with 10 percent by weight of

66° clear water-white sulphuric acid. The aniline should be pure water-white material.

A 300 gal. autoclave is charged up with 600 lbs. of aniline and 600 lbs. of methyl alcohol to which 60 lbs. sulphuric acid has been previously added. The autoclave is capped up and the oil bath gradually heated to 190° C. The pressure rises to about 400 lbs. From this point the temperature is slowly raised to 200° and maintained at that point for 6 hours. As the reaction takes place in the vapor phase, ample free board should be left in the autoclave and oftentimes columns are placed on the heads to facilitate the reaction. On top of such columns control connections can be made for pressure gauges, safety valves and release lines.

At the close of the cooking period the autoclave is first cooled somewhat and then the release line is opened and the excess methyl alcohol, together with ether, is led to a series of condensers for the recovery of the alcohol, the ether being washed in a water column before being liberated into the air. The pressure is thus reduced to 100 lbs. before shutting the release. The blowline is now opened and the charge transferred through a series of coolers under its own pressure to a jacketed neutralizing kettle, the vent of which leads to the same condenser system previously noted. This is prepared with sufficient caustic solution to hydrolyze the contents of several autoclave charges. If the autoclave charge is not transferred hot, it is allowed to cool until the following day and then drawn by suction into the neutralizing kettle. The neutralization is carried out under a pressure of about 100 lbs. in order to decompose the sulphuric acid salts which are hydrolyzed only with great difficulty. The charge is then drawn into the still.

The stills are quite large, capable of holding at least five charges. Its construction and arrangement is similar to that used in aniline rectification. When a full charge is in the still, heat is applied to the still jacket or inside coils. The methyl alcohol and ether are distilled off and led through a dephlegmator into the condenser where the alcohol condenses out

and then through a water column where the ether is washed. Live steam is admitted into the still when the rate of alcohol flow slows down and the dimethylaniline and alcohol are carried over with it. The condenser on the dephlegmator controls the temperature of the distillate so that the water and alkylaniline are condensed and returned through a U bend to the still. The alcohol vapors pass through a large secondary lead condenser and the recovered material is delivered after rectification to its storage tank for further use. The distillation should proceed slowly at the fractional point when dimethylaniline starts coming over with the distillate. The condenser on the dephlegmator is then shut off and the vapors are led directly to the large condenser using a down flow passage through it. The distillate is now collected in its own reservoir. The steam supply must now be increased and the dimethylaniline comes over steadily with about fifteen parts of water. Towards the close of the distillation the pressure on the still is brought up by heating the jacket and the charge finished by steaming out under pressure.

The aqueous solution is led to conical bottom tanks where it is salted, agitated, and settled. The clear water is run off first from the bottom through a trough. As soon as traces of dimethylaniline appear the bottom valve is closed and the clear base is taken from an upper draw-off line. This material is again settled in a large blending tank before final rectification in vacuo. The yield by the above process is 122.5 based on 100 lbs. of aniline used. This is 94 percent of Theory.

The purity of dimethylaniline is controlled largely by distillation. It should pass over between 191–193° C.

A catalytic method for preparing dimethylaniline has been patented (Knoll & Co., G.P. 250,236). A mixture of pure aniline (93 parts) and methyl alcohol (96 parts) and iodine (1 part) are heated in an autoclave for seven hours at 230°. The condensation mass is separated from water and the iodine removed with alkali. It is then distilled in a vacuum. A quantitative yield is said to be approximated by this process.

Dimethylaniline * is also made by treating methylchloride with aniline and slaked lime in an autoclave.

A jacketed agitated autoclave, 500 gal. capacity, is used. The agitator is adjusted for a speed of 125 R.P.M. This is charged with 500 lbs. aniline, 400 lbs. quick lime which has been slaked to about 180 gals. and heated to 100° C. Then 620 lbs. of methylchloride are introduced gradually taking four hours to make the addition. The pressure is then brought up by heating through the jacket to 75 to 85 lbs.

At the close of the reaction, the pressure is lowered to 35 lbs. and the charge blown to a still. Steam is used to carry over the dimethylaniline. The yield by this process is 116–120 per 100 lbs. aniline used.

Dimethylaniline boils at 192.6° and melts at 0.5°. It has a specific gravity of 0.96 at 15°. Its solubility in water is much less than that of aniline which makes possible a direct separation of the aqueous liquor from the distillate tank.

It is used for the manufacture of Butter Yellow, Diazine Green S, Methyl Orange, Auramine, Malachite Green, Victoria Green 3 B, Azo Green, Methyl Violet, Crystal Violet, Methyl Violet 5 B, Methyl Green, Fast Green, Napthalene Green V, Methylene Blue, Methylene Green O, Thionine Blue G.O.

DIETHYLANILINE

$N(C_2H_5)_2$

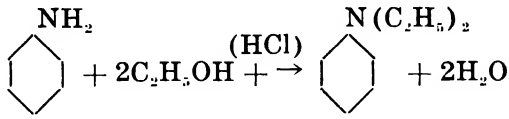
Production	Lbs. Made	Prices
1918	48,048	$2.55
1919	30,000	.88
1920	180,542	1.36
1921	32,812	.97
1922	42,040	
Total	333,442	
Annual Average	66,688	

Aniline used in industry annually, 50,000 lbs.

* Grandmougin, Rev. prod. Chim., 1917, 20, 68.

Process Involved: *Condensation—Hydrolysis.*

Reaction:



Preparation:

Preparation

The manufacture of diethylaniline is similar to the process employed in preparing dimethylaniline. Due to its tendency to form a high percentage of ethyl ether, sulphuric acid obviously can not be used as a catalyst. Hydrochloric acid has been used successfully but modern practice rebels at the use of so corrosive a material, its action on the steel autoclaves used being considerable. The introduction of salts of bromine (e.g., ethyl bromide) and iodine have proven to be satisfactory substitutes for hydrochloric acid in carrying on the reaction, their use resulting in the production of a mixture of monoethylaniline and diethylaniline of varying proportions. This fact is no serious obstacle, however, as the separation of diethylaniline in a pure state is accomplished very economically by benzylating the finished autoclave mixture after neutralization, with benzyl chloride. This practice produces ethylbenzylaniline in addition to diethylaniline. The diethylaniline being a saturated tertiary amine remains inactive while the monoalkyl combines molecule for molecule (see ethyl benzyl aniline) with the benzyl chloride used.

The mixture of ethyl and diethyl anilines are treated in a jacketed agitated kettle with benzyl chloride, an excess of about ten percent (10%) over the theoretical combining weight being used. A calculated quantity of either sodium acetate or sodium carbonate is added as catalyst in order to take up the HCl liberated during the reaction—

$$C_6H_5NH \cdot C_2H_5 + C_6H_5CH_2Cl = C_6H_5N(C_2H_5)CH_2C_6H_5 + HCl$$

The charge is refluxed at 102° C. for six hours. When the conversion is complete, live steam is introduced into the reaction

kettle. Diethylaniline, which is volatile with steam, is carried over to a receiver while the ethylbenzylaniline remains behind and is purified by distillation in vacuo.

The preliminary reaction is carried out in jacketed autoclaves which are heated with circulated oil for eight hours. Machines of 300 gallons capacity designed for this purpose are made of rolled steel and tested to 1,800 pounds pressure.

When hydrochloric acid is used as a catalyst the procedure is as follows: 700 pounds of dried aniline salt (equivalent to 500 pounds pure aniline) are added to 800 lbs. of ethyl alcohol in a small mixer. The mixture is agitated and the slurry delivered to the autoclaves. The temperature is brought up very slowly to 200° C., the pressure corresponding being about 800 pounds per square inch. The charge is cooked for eight hours, and then cooled down so that it can be drawn into the neutralizing kettle where it is treated under pressure with caustic soda. Here the excess alcohol is distilled off after making the charge alkaline with 600 pounds of thirty percent (30%) sodium hydroxide solution. The diethylaniline is distilled over into conical bottom reservoirs where the alkyl base is salted out, and after running off the water it is transferred to vacuum stills; or it may be benzylated as described above.

About one percent of iodine may be added to the autoclave charge to facilitate the conversion, this being removed by treating with sodium hydroxide in the neutralizing kettle.

Paratoluene sulphon chloride may be added to the alkaline mixture. The monoethylaniline * is thus converted into the toluene sulphon derivative, which is not volatile with steam, so that the diethylaniline may be distilled over quite pure.

One of the customary methods of preparation is to put 500 pounds of aniline oil into an enamel-lined jacketed kettle provided with water and steam connections. The oil is heated to 100° C. at which time 600 pounds of ethyl bromide are run in slowly permitting the temperature to rise to 130° C.–140° C.

* Fierz David, Dye Chemistry.

The charge is heated for four hours at 130° C. and blown to a still where it is neutralized with caustic and then steam distilled. The oil brought over with the steam is separated from the water, and 300 pounds of it are again put back into the kettle along with 200 pounds of good diethylaniline. The temperature of the batch is raised to 100° C. when 300 pounds of ethyl bromide are run in slowly keeping the temperature at 130° C. by means of cold water circulated through the jacket. Cook for nine hours at the above temperature after the ethyl bromide has been introduced. The charge is then blown to a still, neutralized and finally distilled with steam.

Another process for the preparation of both ethyl- and diethylaniline involves the reaction of aniline with diethylsulphate. This process has at present only academic interest but is fraught with possibilities if the cost of the alkyl content of this intermediate can be brought in line to compete favorably with pure alcohol.

This process * is described by Cade as follows:

"*Mono- and Di-ethyl Anilines.*—The ethylation of aniline by means of diethyl sulphate is characterized by quickness and completeness of reaction, ease of manipulation and relatively low costs. No autoclaves are necessary, no high pressures are developed, the time required for the reaction is small and the working up of the material is fairly simple. All that is necessary is a closed vessel, fitted with a tight reflux apparatus and working under atmospheric pressure. With proper precautions as to temperature control and stirring, even the reflux apparatus is not necessary.

"It has been found that the simple expedient of adding dry hydrated lime to aniline and then treating this mixture with diethyl sulphate and heating makes it possible to utilize both ethyl groups of the diethyl sulphate to alkylate the aniline and practically pure diethylaniline can be prepared in this manner. When no lime is used—that is, when 1 mol of aniline is added to

* Industrial Fellow, Mellon Institute of Industrial Research. Reprint by courtesy Carbide and Carbon Chemicals Corporation.

1 mol of diethyl sulphate—the reaction ensues unassisted. Considerable heat is developed and it is necessary to keep the mixture well stirred and the temperature controlled at 55 to 85° C. The reaction is over in a few minutes time, although it is recommended that the mixture be kept stirred for a period of ½ to 1 hour in order to insure complete reaction. At the end of this time the mixture has become viscous. It is then taken up in a little water, in which it is completely soluble. The solution is then made alkaline with caustic soda. This causes the ethylated anilines to separate out as an oil which floats to the top and which can be separated off and redistilled, or steam distilled, as desired. Theoretically the reaction involved is as follows:

$$C_6H_5NH_2 + (C_2H_5)_2SO_4 = C_6H_5NHC_2H_5 + C_2H_5HSO_4$$
$$= C_6H_5NHC_2H_5, C_2H_5HSO_4$$

Actually the aniline is not all converted to monoethylaniline, a small amount of the monoethylated product being converted further to diethylaniline and, as a result, an equivalent amount of unused aniline remains.

" In this latter process only one ethyl group of the diethyl sulphate is utilized in ethylating the aniline. This is due to the fact that the second ethyl group becomes bound up as ethyl hydrogen sulphate and forms, as such, a double salt with the base. Heating this double salt at relatively high temperatures (around 185° C.) did not bring about a molecular rearrangement and thereby make available the second ethyl group. Even higher temperatures were tried out in order to bring about this desired rearrangement, but such usually caused a general decomposition of the material.

" *Diethylaniline.*—To prepare pure diethylaniline and at the same time utilize both ethyl groups of the diethyl sulphate the following process was found very satisfactory. Several factors such as temperature, time of heating and concentration of reacting materials can be varied in many different ways to give a variety of results. All cannot be discussed in detail here. The following detailed outline will give the best general method as a

basis, which can be made use of and varied at will by those interested to meet their specific needs.

"To 1 mol of aniline, which was contained in an iron vessel provided with a stirring device, thermometer well and reflux condenser, was added 1.2 mols of dry powdered calcium hydrate. This mixture was then well stirred and 1.1 mols of commercial diethylsulphate added, the addition being made in 4 or 5 portions spread over an interval of ½ to 1 hour's time. About 5 minutes after the addition of each portion of diethylsulphate the temperature of the batch began to rise quite rapidly, and it was found that this rise must not be allowed to go beyond 85° C. When this temperature peak had been reached and the thermometer showed a lowering again, then the second portion of the diethylsulphate was added, continuing the addition in this manner until all had been added.

"After the last heat rise had begun to subside the vessel was heated externally and the temperature of the mass brought up to 110–115° C. At this point considerable amounts of steam were evolved, and the vapors were allowed to pass through the upright reflux condenser, thence through an inclined condenser—water cooled—in order to collect the small amount of partly ethylated aniline that was mechanically carried over with the steam. This oil was separated from the water and returned to the reaction mass. The temperature was then gradually raised to 145° C. and maintained there for 4 hours. Thorough stirring was continued during the entire process.

"After this 4-hour heating the mass was steam distilled and the ethylated aniline thus obtained analyzed approximately 90 percent diethylaniline and 10 percent monoethylaniline. No trace of unused aniline was present as shown by the sulphuric acid test and also by the zinc chloride test. The heat rise of the mixture, caused by the addition of 5 cc. of acetanhydride to 5 cc. of the ethylated aniline, was 9 to 10° C.

"When 1.4 mols of diethylsulphate was used instead of 1.1 as just described, the final product analyzed 98 percent diethylani-

line or better. The yield of the ethylated product in either case was 90 percent or better on the basis of the aniline used.

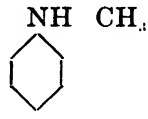
"It will be noted that an excess of diethylsulphate is called for in the latter case where a practically pure diethylaniline is prepared. This is partly due to the fact that the commercial grade of diethylsulphate was only 94 to 96 percent pure, and partly due to equilibrium considerations. It is probable that longer heating would produce the same effect with less diethylsulphate.

"It would thus seem that the above method is the best and least troublesome one for the preparation of diethylaniline. The diethylsulphate may be handled with caution, no recovery processes are necessary, as is the case where ethylbromide is used, and no pressure equipment is necessary."

Diethylaniline melts at —38.1, boils at 216.5 and has a density at 18 of 0.939.

It is used for making Brilliant Green, Patent Blue V, Ethyl Purple, Acid Violet, Xylene Blue Vs, Cyanine B and Amethyst Violet.

METHYLANILINE



This intermediate is usually prepared by the Morgan process* as follows: Sixty parts of aniline and sixty-six parts of 40 percent formaldehyde are added slowly and concurrently to 300 parts of 34 percent sodium hydroxide solution which contains 90 parts of zinc dust in suspension. The addition of the reagents should take about two hours, and the mixture should be thoroughly stirred maintaining the temperature at 90°. Forty parts of 40 percent formaldehyde are slowly added during the course of the next six hours, the temperature being maintained at the required point. The mixture is distilled with steam and the methylaniline separated out from the distillate. The crude product is rectified and put into drums.

* English Patent 102,834, U. S. Patent 1,221,077.

with oil or alloy. Agitators are used whenever the reaction mass is such that it separates out in layers. When the contents are homogeneous as in the manufacture of diphenylamine or dimethylaniline stirring apparatus is not necessary. Alkali fusions, however, require a stirring mechanism in order to obtain the best results and to prevent charring of the charge. Iron, cast steel or rolled steel autoclaves are now on the market. For high pressure work the latter are found to be more satisfactory from a safety standpoint. The rolled steel autoclaves may be hammer welded or lap welded and rolled, and are found to be very satisfactory as there is practically no possibility of finding flaws in them such as are found in castings. Modern welding or rolling technique is such that machines of this type have been used for ten years continuously without giving any trouble whatsoever.

The autoclaves are hollow and cylindrical with a wall thickness calculated to withstand the pressures required by the chemical manufacturer. The design giving maximum strength calls for hemispherical bottoms and very heavy top flanges to which the cover is bolted. The top flange extends out from the body of the autoclave to permit of making a broad contact surface for the bolts and nuts used in making the flange tight. It has been found that the tongue and groove joint stands up better than the customary flat-faced flange union. As the success of the autoclave operation depends on absolutely tight joints, the cover should be provided with a sufficient number of bolt holes and only the best hand-forged wrought iron bolts used.

A number of materials can be used in the groove for making the cover or charging flanges tight. Asbestos is the cheapest and probably the most satisfactory article. It can be obtained either in the form of a cut gasket made of compressed long fiber or as a graphited braided coil. The latter is flattened out to fit the groove and the ends lapped over. Joints made with the above materials have been tested and used at 800 lbs. per square inch and found satisfactory. Copper, silver and lead are also used extensively. In fact for some operations a

metal gasket proves economical if the flanges have to be removed quite frequently. Flat asbestos gaskets which are properly graphited can be used several times before being thrown away. As a rule there is less danger of leaks where asbestos is used in preference over the metallic gaskets.

The technique of tightening down flanges is to screw down on opposite sides until a slight pressure is developed and then to continue in a circle, always screwing up tighter and tighter. At some plants six foot extensions are put on the wrench handles in order to effect the final pulling down.

Provision must be made in the design of the autoclave for the use of a thermometer, pressure guage, safety valve, emergency release lines and a blow leg. Sometimes all of the above connections are placed on the cover, while some machines are designed so that the safety line, pressure gauge and release line are attached to a header on the cover, the charging and discharging connections being made by separate flanges on the autoclave body proper.

The autoclave is usually set into a framework of masonry contained in a steel shell. A large movable crane is provided to take out and to replace the machines. This duty should be performed at frequent intervals as all autoclaves are subject to both erosive and corrosive action, and thus require periodical cleaning and examination. At some factories special calipers are used to determine the thickness of the walls of the apparatus during this periodical inspection, and definite limits set beyond which it is considered unsafe to operate the machine. The heating of autoclaves in modern plants is usually done with oil, although electric heating has been adopted in some plants for particular condensations.

Heating with oil is accomplished either by direct fire or through the medium of an oil circulating system. The fire from the fuel oil burner is never directed at the autoclave as such a procedure would result in local overheating and cause bulges in the base of the machine. Some works use a pier of masonry underneath the apparatus to deflect the flame around the sides,

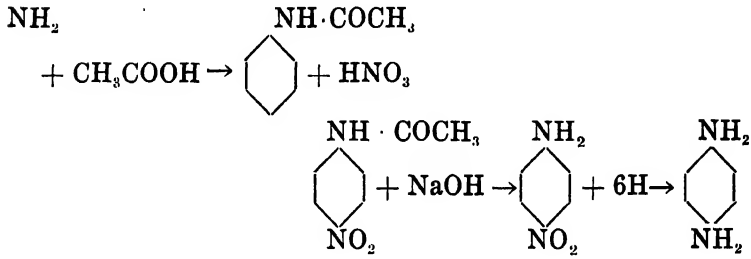
others use a Dutch oven design in which the fire is directed at the bottom of the combustion chamber while a baffle wall, extending back almost to the rear, separates the flame area from the casting. The heating in the latter case is done largely by the masonry which has been brought up to a glowing redness. The shell surrounding the autoclave is provided with observation holes which are used not only to examine the apparatus during normal operations, but also to cool down the setting after a run is completed. Compressed air or steam is often blown into the combustion chamber to expedite the cooling. The control of the operation is effected by the use of thermometers and pressure gauges. The thermometer well should at all times be sufficiently long to extend close to the base of the autoclave as it has been found that oftentimes serious discrepancies exist in non-agitated autoclaves between the lower and upper levels of the charge. Recording thermometers give a more satisfactory report of actual conditions than the ordinary mercury thermometer; such automatic recorders are as a rule not quite so accurate, and oftentimes give considerable trouble; their use however is conducive to better operating control. All thermometers should be checked up at frequent intervals against a standard instrument. The pressure gauges should be placed so that they are visible to the operator at the burners in order that immediate action can be taken in the event of sudden rise in temperature. The piping leading to the gauge should be started at the highest possible point to guard against stoppage of the line by part of the charge. This line should contain a U bend filled with oil just before the gauge. The gauges should be tested out periodically with a test instrument. A log should be kept of every charge showing the temperature and pressure condition at frequent intervals. From the log the supervisor can determine whether the standardized conditions have been adhered to.

By the use of new automatic devices temperatures and pressures can be controlled automatically. It is advisable, however, that the autoclave room be provided with the usual operator to check up on operating conditions.

Such operators must be carefully trained, and should not be thrown on their own responsibility for a long time. Rules and regulations should be printed and posted and a copy given to every new operator so that chances for accident are cut down to a minimum.

Nitrations and Reductions

Acetanilide
P. Nitroacetanilide
P. Nitroaniline
P. Phenylenediamine



PARANITROANILINE

Production	Lbs. Made	Price
1918	1,320,064	$1.30
1919	1,310,658	1.06
1920	2,138,492	1.17
1921	832,438	.85
1922	1,563,665	.68
Total	7,165,317	
Annual Average	1,433,063	

Amount aniline used in industry—1,350,000.
Processes involved: acetylation, nitration, hydrolysis and reduction.

Reactions:

Acetylation—$C_6H_5NH_2 + CH_3COOH \rightarrow C_6H_5NHOCCH_3 + H_2O$
Nitration—$C_6H_5NHOCCH_3 + HNO_3 \rightarrow C_6H_4NO_2NHOCCH_3 + H_2O$
Hydrolysis—$C_6H_4NO_2NHOCCH_3 + NaOH \rightarrow C_6H_4NO_2NH_2 + CH_3COONa$
Reduction—$C_6H_5NO_2NH_2 + 6H \rightarrow C_6H_4(NH_2)_2 + 2H_2O$

Manufacture:

Preparation of Acetanilid.—This is accomplished in a jacketed aluminum kettle 500 gal. capacity, the inner walls of which are about one half inch in thickness. The jacket permits of heating by a circulating oil system. The acetylating pot is provided with a cover which can be used for frequent inspection of the inside lining. Connections are also made in the kettle for inlet pipes to receive the charge, standpipe for discharging, air connections for blowing, thermometer well, pressure gauge and a large outlet for the vapor line which leads to a water-cooled condenser. The piping wherever possible is silver lined or made of aluminum. The condenser is arranged for distilling or refluxing.

The following proportions may be used: 1,600 lbs. of aniline and 1,640 lbs. of glacial acetic acid are blown into the aluminum acetylator. The kettle is arranged so that the distillation line is open while the temperature of the charge is brought up to 120° C. by starting the oil circulating system. About one hour is required to reach this temperature at which time the reflux line is brought into operation and the charge cooked for twelve hours. The operation runs very smoothly as the temperature automatically remains almost constant, the heating system controlling only the rate of distillation. The temperature is now brought up to 130° by distilling for one hour. The charge is again refluxed for 6 hours after which the temperature is finally raised to 150° and then, after one hour, blown to the wooden quenching tub. The acetylation thus takes about 24 hours for completion.

	Strength of Acetic Acid Distillate
Loading, 1/2 hour	
Bring to 120° C., 1 hour	20% to 30%
Reflux at 120°, 12 hours	
Raise to 130°, 1 hour	35% to 45%
Reflux at 130°, 6 hours	
Raise to 150°, 1 1/2 hours	60% to 70%
Blow and cool, 2 hours	
Total cycle, 24 hours	

During the distillation periods, about 600 lbs. of weak acetic acid ranging in strength from 20 percent to 70 percent is distilled off, the strength increasing with each successive distillation. The recovered acid which is from 26 to 28 percent of total used, analyzing 35 percent, may be converted into sodium acetate, to copper acetate for Paris green manufacture, or used in the neutral reduction of certain nitro-compounds.

The yield per 100 lbs. of aniline used should be 140 or 2,100 lbs. of acetanilid for the 1,600 lbs. aniline charge. Some authorities* claim a yield of 143 to 144 for this operation although such good yields are as a rule not obtained in American plant practice.

The blowline from the acetylator discharges into a wooden quenching tub about 6 ft. in diameter and 6 ft. deep. In this tub 20″ of water (350 gals.) at 65° is run and this is agitated by means of a stirrer penetrating the cover.

In some plants the batch from the acetylator is delivered to iron crystallizing pans and allowed to cool. This acetanilid is broken up the following day and ground in a mill. The para-nitroaniline obtained from this product is not quite as bright as that derived by the former process.

The warm water in the quenching tub prevents the formation of any hard lumps while the charge is coming in. The agitator is kept running until the charge has cooled down to 10°. The cooling is often facilitated by bubbling through air for ten to fifteen hours. It is then centrifuged and washed until free of acetic acid. The press cake is finally taken to the dry house where after drying it is brought back as grayish-white, scaly crystals for sulphonation.

Preparation of Nitroacetanilid

Nitration:

A standard nitrator (see illustration) possessing a very efficient stirring design is used for the preliminary sulphona-

* Fierz David.

tion and final nitration of the acetanilid. The nitrator is equipped with brine coils for controlling the reaction temperature.

1,000 lbs. of dry acetanilid is fed very slowly into four times its weight (4,000 lbs.) of 66° clear white sulphuric acid. The temperature during the feed is kept at 25° C. to prevent hydrolysis, the operation consuming from three to four hours. At the close of the feed the material is in solution and is ready for the nitration acid after first cooling to the nitration temperature. The sulphuric acid acts as a dehydrating agent and here also facilitates mononitration and prevents oxidation products. The charge is now cooled to 2° C. and then 750 lbs. of 66° sulphuric (92.5 percent) and 700 lbs. of 42° Bé. nitric as mixed acid are very slowly fed in the nitrator, the temperature being controlled by means of the brine coils or jacket at 1° to 3° C. When the mixed acid is all in, the charge is stirred for one hour longer, the entire operation consuming from 10 to 12 hours. Care must be exercised that the temperature of the mixture shall not go below 1° for a lower temperature produces a covering of ice on the inside of the nitrator which acts as a non-conductor and retards the cooling of the batch, consequently delaying the acid feed. If the temperature exceeds 3°, considerable ortho may be formed. A sample from the nitrator is taken and poured on ice and the nitro-acetanilid filtered and washed with cold water. The precipitate is hydrolyzed in a test tube with dilute caustic soda solution, a clear yellow solution should result. If the acetanilid has not been completely nitrated an odor of aniline may be detected.

Some plants divide the nitration operation into two parts. Then 500 lbs. of acetanilid is slowly stirred into 2,000 lbs. of 66° Bé. sulphuric in a 300 gal. sulphonating pot. The temperature is controlled as above at 25° C. by means of a brine coil. This charge is kept in the sulphonator until the nitrator is ready to receive it.

The batch from the nitrator is run out at the bottom outlet into a round suction filter containing 600 gallons of water and

sufficient chopped ice to keep the temperature below 15° C. This filter is a large wooden tub 8′ in diameter having a false bottom of filtros tile. It is provided with a stirrer which is set in motion when the charge from the nitrator is to be run into the ice and water. The ice used in this operation is just enough so that only a few lumps remain unmelted when the precipitation of the para (and ortho) nitroacetanilid is complete. The nitroacetanilid which is brown as it runs from the nitrator turns pure milky white when it hits the iced water. If the P. nitroacetanilid is to be sold as such, it is now washed on the filter twice with cold water and the remaining acid neutralized with 100 to 200 lbs. of 3.5 percent caustic soda solution. The neutralized cake is washed once more to remove the excess of caustic and then dumped and dried. For paranitroaniline production, the cake, after being washed, is transferred to the hydrolyzing kettle and mixed with 600 gallons of water, which is just enough to make the mass sufficiently fluid to mix. The filtration and washing is completed in 7 to 8 hours.

Any orthonitroaniline can be separated on the suction filter by making slightly alkaline with 2 or 3 lbs. of 35 percent caustic and heating up to 80° C. with a small quantity of water. This liquor containing the hydrolyzed ortho is then filtered off.

In some plants the nitrator batch is first run into a wooden lead-lined tub containing the chopped ice and water. From here it is run by gravity after neutralization into a blowcase and subsequently blown on to a plate and frame filter press. In this press the ortho can be removed by continued washing with warm water at 18° C.

The yield of nitroacetanilid is 85–88 percent of theory based on acetanilid; when sold as such it is dried in vacuo at 60° and ground.

Hydrolysis of Paranitroacetanilid to Paranitroaniline

The hydrolysis of the acetyl derivative is nearly always carried out with soda lye. As a rule several nitration charges are delivered to large cast-iron, agitated kettles, used for this pur-

pose. These kettles are often jacketed, and are always covered in order to prevent the noxious fumes from escaping into the house. Flues are provided on top of the tub to draw off such fumes. The kettles may also be provided with coils for the preliminary heating and final cooling of the batch.

The kettle for a nitration batch (1,000 lbs. acetanilid) is prepared with 300 gallons of water and 1,200 pounds of 35 percent caustic solution, which is fed in simultaneously with the nitroacetanilid. This is slightly in excess of actual requirements as the solution should be strongly alkaline during the hydrolysis. The hydrolysis is carried on by heating with steam circulating in the coils in the tub, the charge being kept at an incipient boiling for two hours.

The paranitroacetanilid is fed into the kettle only after the solution is brought to boiling, and the reaction starts immediately. The milky white paranitroacetanilid turns yellow and remains as a dense flocculent suspension during the boiling while the solution becomes reddish brown. Samples are taken near the close of the boiling period and when a clear solution is obtained by dissolving some of the suspended paranitroaniline in HCl, the operation is considered complete. Cooling water is now admitted into the coils in the kettle and the batch cooled to 40° C. It is then filtered in a large centrifuge. The yellow cake is then washed with cold water until the waters run clear, after which it is removed to the dryhouse and dried either in vacuo or with hot air. The dry powder is finally pulverized in a ball mill, the balls being made of hard wood. The appearance of the finished product improves by milling to a very fine powder.

The product must give a clear solution in hot dilute hydrochloric acid. Its diazo solution should be clear and yellow. Paranitroaniline made by the autoclave process from paranitrochlorbenzene although much purer will yield an opalescent diazo solution. So this point cannot be accepted as a criterion for judging the quality of the finished paratoners. The melting point should be 147° to 148° C.

The yields obtained in this process range from 105 to 108 lbs. per 100 lbs. of aniline used for good factory operations. The cost of the finished product may be somewhat reduced by recovering the waste acid from the nitration operation, and by utilizing the by-product sodium-acetate solution for the preparation of a commercial product by evaporating it down in a concentration plant.

Paranitroaniline is used extensively for the production of Para Red, on the fibre, for the manufacture of Paraphenylenediamine, and Napthol Blue Black. According to a recent patent (U. S., 1,415,704) paranitroaniline when diazotized and coupled with " S " acid, and then reducing the nitro groups thus obtained, will yield a new union dye, suitable for dyeing silk, cotton or wool, as well as mixtures of such fibres. It produces in general greenish black shades, and is capable of being diazotized directly on the fibre of the fabric with beta-napthol, m. phenylenediamine, m. tolylenediamine and so forth, to give reddish to green shades of black.

A list of dyes derived from paranitroaniline follows:

Azo Cardinal G
Nitrophenine (Thiozol Yellow R)
Apollo Red B
Brilliant Archil C
Paranitroaniline Red
Chromotrope 2B
Alizarin Yellow R
Victoria Violet
Azo Acid Blue B
Blue Black N
Domingo Blue Black B
Napthol Blue Black
Nigrophor B A S F
Anthracene Acid Brown G
Nyanza Black B
Azophor Blue D
Diamine Black H W
Diamine Green B
Diamine Green G
Thional Black

PARAPHENYLENEDIAMINE

Production	Lbs. Made	Price
1918	215,148	$3.68
1919	234,332	2.42
1920	?	?
1921	124,954	1.70 sales
1922	342,111	1.39
Total	916,545	
Average	229,136	

Process Involved: Reduction.

Reaction: (See Aniline.)

$$C_6H_4NO_2NH_2 + 6H \rightarrow C_6H_4(NH_2)_2 + 2H_2O$$

Preparation:

Paraphenylenediamine is manufactured commercially by the reduction of paranitroaniline. This reduction is quite similar to that of nitrobenzene to aniline and its technique is also subject to some of its numerous modifications. One thousand pounds of paranitroaniline is gradually fed into a large agitated wooden tub in which 1,000 lbs. of iron and 200 lbs. of 30 percent HCl have been previously mixed with a large volume of water and brought to a boil. The rate of feed is such that no marked pressures are developed. The reaction gases are led from the reducer by means of a tall wooden flue. Adjustments of iron and acid are made during and at the close of the feeding period so that the charge will be reduced in the required time. The usual color test is made by dropping some of the reduction liquor on filter paper to insure complete conversion of the paranitroaniline. The charge is finally neutralized and filtered. The press cake is washed clear of any valuable diamine by washing first with weak wash waters and finally with fresh boiling water. The cake is finally dried with an air blast after which it is dumped from the press.

The liquor which contains the soluble paraphenylenediamine is run into a storage tank from which it is subsequently delivered to evaporators and concentrated to 40° Bé. before transfering to a vacuum dryer. The crude product from the dryer can then be either recrystallized in hot water or distilled in vacuo.

Paraphenylenediamine is also made from aminobenzene as obtained in the outlined method of preparation. (See page 200.) The contents of the lead-lined pan (before separating the aniline) are blown into a standard cast iron jacketed reducer, similar to that used for the manufacture of aniline. The reducer is prepared as in the case of reduction of paranitroaniline with water and about 80 percent of the iron borings and

hydrochloric acid necessary to effect the reduction. Reduction begins as soon as the aminoazobenzene comes in contact with the iron and the temperature rises gradually to 30° – 40° C. Stirring is continued for several hours and final additions of iron borings and acid are made until the charge becomes colorless. The charge is now made alkaline and steam is admitted into the

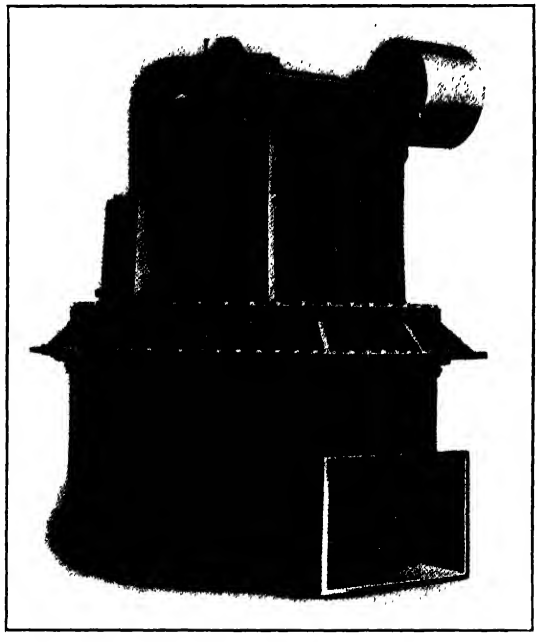


FIG. 24.
8 Ft. Extra Heavy Vacuum Still.
Steam- or oil-jacketed. Capacity 1600 gallons. (Bethlehem Foundry Manufacture.)

jacket and introduced into the solution through the hollow core of the agitator (or other steam connections) and the excess of aniline distilled off and recovered. The entire charge is then filter-pressed, and the cake on the leaves washed thoroughly with hot water and blown with air.

The yield obtained by this method of preparation is about 85 percent of theory based on the sodium nitrite used. Some authorities believe it a more economical method of preparation.

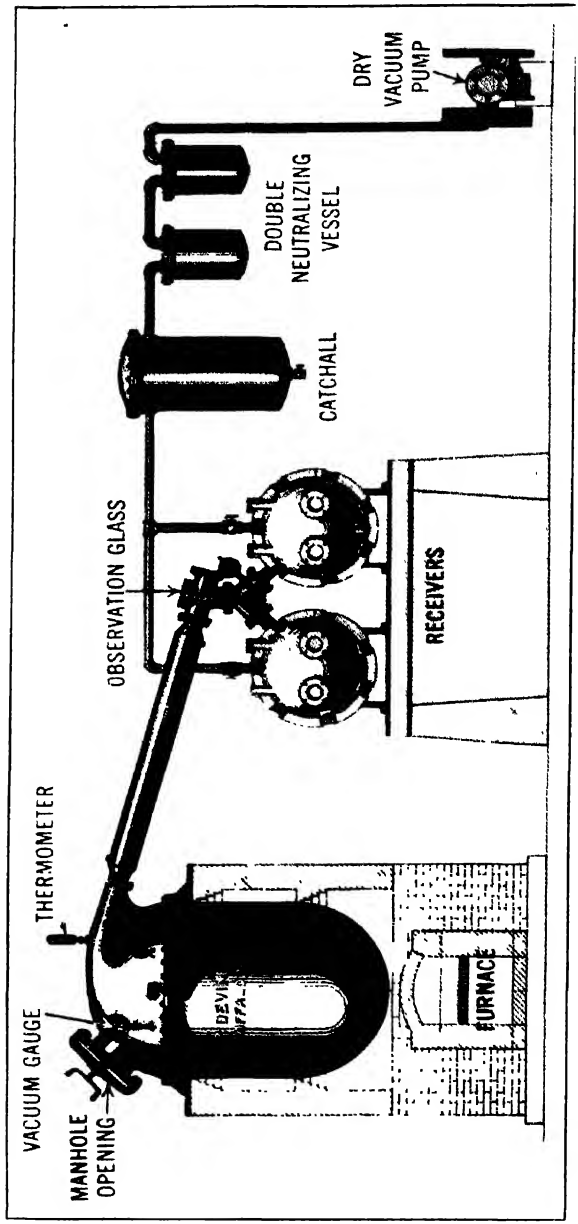


FIG. 25.
Vacuum Distillation System.
For purifying materials that solidify at comparatively high temperatures, e.g. p. phenylenediamine and beta naphthol.

Paraphenylenediamine melts at 141° C. and boils at 267° C.

This dyestuff finds its greatest market among the fur dyers for developing " Hudson Seal " from Australian rabbit skins. In Japan it is used alone or with Fuscamin to obtain a characteristic fast black for cotton printing. It has been used quite extensively in the rubber industry and is regarded as one of the rapid accelerators. Small quantities of it have been incorporated in hair dyes—but its tendency to produce rashes should make this practice objectionable.

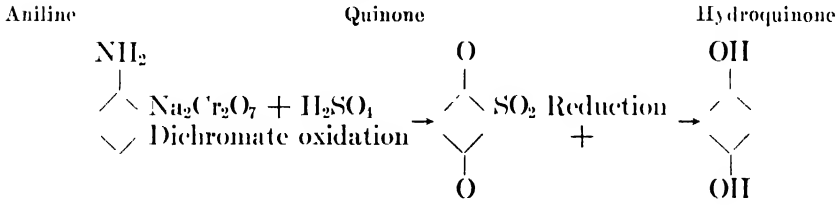
The following dyes are derived from P. Phenlyenediamine:

Polychromine B	Isodiphenyl Black R
Victoria Violet	Cresyl Blue 2 BS
Diphenyl Chrysoine R R	Paraphenylene Violet
Diphenyl Catechine G	Paraphenylene Blue R
Diphenyl Fast Brown G	Para Blue
Leather Brown	Thiofor Bronze 5 G
Violet Black	Thiophor Yellow Bronze C
Azo Alizarin Bordeaux W	St. Dennis Black B
Azo Alizarin Black 1	Auronal Black B
Columbia Black F F	Ursol D, D B

Oxidation and Reduction Processes

Quinone

Hydroquinone



Quinone, the oxidation product of aniline, has very limited commercial importance. It is made in comparatively large quantities, however, for reduction to hydroquinone which is used extensively as a developer in the photo-chemical field.

Hydroquinone is prepared usually by the oxidation of aniline to quinone, and then by reducing this intermediate by treatment with SO_2.

Oxidation Aniline to Quinone:

Preparation: A mixture containing 25 parts of aniline—200 parts sulphuric acid (water white) and 600 parts of water are cooled by ice in a wooden vat. A solution of 25 parts sodium bichromate in 100 water is slowly added and the agitation continued for 12 hours. An additional 50 parts of sodium bichromate in 200 parts of water are then added and the agitation continued until the oxidation is complete. The temperature during the whole reaction must be kept below 5° C. by the addition of ice. If the solution is permitted to stand the quinone will rise to the surface and can be skimmed off and purified.

Reduction Quinone to Hydroquinone:

Preparation: SO_2 gas is now introduced into the charge in the reaction tub until the smell of it remains in the solution. The resulting hydroquinone is then extracted by ligroin or other selective solvents. Owing to its easy solubility in water (5.85 parts per 100) this extraction offers considerable difficulty. The extract must be recrystallized from water (using bone black to decolorize it and a little SO_2 to prevent oxidation) in order to make it satisfactory for use.

Hydroquinone crystallizes in colorless prismatic crystals, melting at 169° C. It reduces ammoniacal Ag solutions when warmed and Fehling's solution in the cold.

According to a recent patent, U. S. P. 1,421,869, hydroquinone is prepared by sulphonating para dichlorbenzene, and later treating sodium para dichlorbenzenesulphonate with caustic soda. The free alkali is then neutralized with hydrochloric acid.

One hundred (100) parts of p. dichlorbenzene are treated with two hundred (200) parts oleum at a temperature of 130°–140° C., maintaining vigorous agitation for one hour. One of the hydrogens of the ring is replaced with a SO_3H group. The

solution is poured into three hundred (300) parts cold water and any unconverted p. dichlorbenzene can be distilled out with steam if necessary. To this solution seventy-five (75) parts of sodium chloride are added. A double decomposition takes place; sodium p. dichlorbenzosulphonate being precipitated, while the free HCl remains in solution.

The precipitate is separated and treated in an autoclave with 225 parts of water and 150 parts of caustic soda at a temperature of 175°–200° C. for twenty-four hours. The autoclave melt containing the sodium salt of hydroquinone is transferred to a neutralizing tub, where it is treated with hydrochloric acid until slightly acid. The solution is first boiled for a few minutes and then cooled, after which the hydroquinone is extracted with ether, or any other suitable solvent. The solvent is recovered by distillation, leaving the hydroquinone, which may be further purified if desired.

Diazo and Azo Compounds

AMINOAZOBENZENE

Production	Lbs Made	Price
1918	171,594	$1.07
1919	82,755	0.72
1920	152,310	0 97
1921	49,763	1.20
1922	153,968	0.63
Total	610,390	
Average Annually	122,078	

Aniline consumed for industry, approximately 90,000 lbs.

The reactions involved are:

$$\underset{\text{aniline}}{C_6H_5NH_2} + HCl \rightarrow \underset{\text{aniline hydrochloride}}{C_6H_5NH_2 \cdot HCl}$$

$$C_6H_5NH_2 \cdot HCl + HONO \rightarrow \underset{\text{diazobenzene chloride}}{C_6H_5N = N - Cl} + 2H_2O$$

$$C_6H_5N = N - Cl + H \cdot HNC_6H_5 \rightarrow C_6H_5N = N - HNC_6H_5 + \underset{\text{diazoaminobenzene}}{HCl}$$

$$C_6H_5N = N - HNC_6H_5 + H \cdot C_6H_4NH_2 \rightarrow C_6H_5N = NC_6H_4NH_2 + \underset{\text{aminoazobenzene}}{C_6H_5NH_2}$$

Discussion:

When an aniline salt is treated with nitrite in the presence of free aniline, diazoaminobenzene is formed. This yellow substance is insoluble in water but soluble in organic solvents. When in solution it is rather stable at low temperatures, but when warmed in the presence of mineral acid a molecular transformation takes place; aminoazobenzene being thus formed from diazoaminobenzene.

The reaction is quite spontaneous but only by following out certain prescribed conditions can a satisfactory product and a good yield be obtained. To procure quantitative conversion it is necessary to treat the diazoaminobenzene while in solution in order to mitigate the action of the mineral acid previously introduced to carry on the diazotization. If in the preparation of the diazoaminobenzene an excess of aniline is used, it acts not only as a solvent for the diazo compound, but combines later with the mineral acid (HCl) so that the latter acts in the form of aniline salt. It is probable that the aniline hydrochloride combines molecule for molecule with the diazoaminobenzene forming an intermediary compound which at 40°-50° C. is unstable, splitting off aniline and leaving aminoazobenzene as a final product of the reaction. In the solution the latter is present partly as free base and partly as salt and by treating the product with an excess of diluted cold acid, the aniline is combined and dissolved while the aminoazobenzene is precipitated as a red salt.

Preparation:

The reaction is carried out in large steel-jacketed kettles which have been enamel-lined to withstand the action of hydrochloric acid. Brine or cold water is circulated during the diazotization as the control of temperature is a very important phase of the operation.

The following proportions may be used—750 pounds of aniline are mixed with 100 pounds of 30 percent hydrochloric acid and the temperature brought to 25° C. Then 50 pounds of so-

dium nitrite dissolved in 150 pounds of water are very slowly added, maintaining the above temperature for two hours after completing the nitrite addition.

The kettle now contains a deep yellow solution of diazoaminobenzene in aniline oil, a small excess of aniline-hydrochloride, and an aqueous solution of sodium chloride. The charge is permitted to settle and separate out into layers. If a large sample run off at the base shows no trace of nitrite, the aqueous NaCl solution is drawn off. When the separation of water is complete, 90 pounds of aniline are introduced into the batch which is now being vigorously stirred. The charge is warmed very slowly so that the temperature rises from 25°-40° C. in six hours. It is then heated further and kept first at 45° C. for two hours and finally at 50° C. for an equal period. As the reaction proceeds, the red azo compound gradually replaces the yellow diazo solution.

When the conversion is complete (as indicated by the absence of a violet ring when spotting for diazo on filter paper wet with one drop of acetic acid solution of a-napthylamine), the charge is run into a covered wooden tub, fitted with fume vent and agitator, containing six hundred pounds of ice and an equal quantity of water. About 900 lbs. of 30 percent HCl are run in until the charge is distinctly acid to Congo. This acidification precipitates out the aminoazobenzene hydrochloride while the excess aniline goes into solution as aniline hydrochloride. The mixture is then filtered through a suction filter or a plate and frame filter with wool cloths. The aniline hydrochloride is led to a lead-lined kettle where it is neutralized with lime and steam-distilled to recover the aniline oil. The hydrochloride of aminoazobenzene is washed on the filter with acidulated brine solution and finally with dilute HCl until free of all traces of aniline. The cake is removed and dried in a vacuum oven at 40°, taking care to avoid overheating.

Aminoazobenzene melts at 127°. It is used for making Fast Yellow, Oil Red O, Cloth Red G, Ponceau 5 R, Azo Acid Violets, Spirit Yellow, Sudan III, Croceine A Z, Croceine B, Brilliant

Croceine M, Benzo Fast Scarlet Induline (spirit soluble), Induline water soluble.

Finished Dyes

DIRECT DEEP BLACK E. W.

(Direct Deep Black V)

Production	Lbs. Made	Price
1919	7,250,007	$1.04
1920	7,736,994	1.03
1921	2,229,842	.79
1922	5,326,457	0.42
Total	22,543,300	
Annual Average	5,635,825	

Aniline consumed annually, approximately, 1,000,000 lbs.

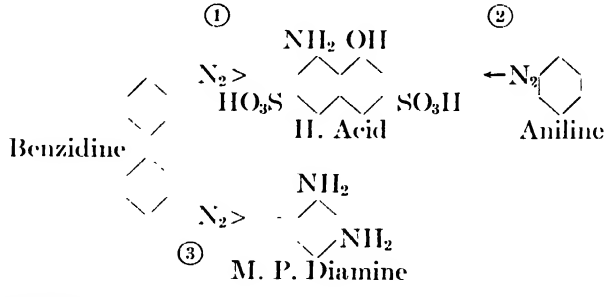
The above azo dyes are the most largely used direct black dyes made in the dye industry. Their application is quite universal as they can be applied to all manner of organic materials.

Processes Involved:

Coupling of diazotized amines.

(a) Benzidine-azo H acid.
(b) Benzidine-azo H acid-azo aniline.
(c) M. Phenylene diamine-azo benzidine-azo H acid-azo aniline.

Reaction:



Manufacture:

The preparation of these azo dyes like all others similar to it is usually carried out in tall brick buildings having at least

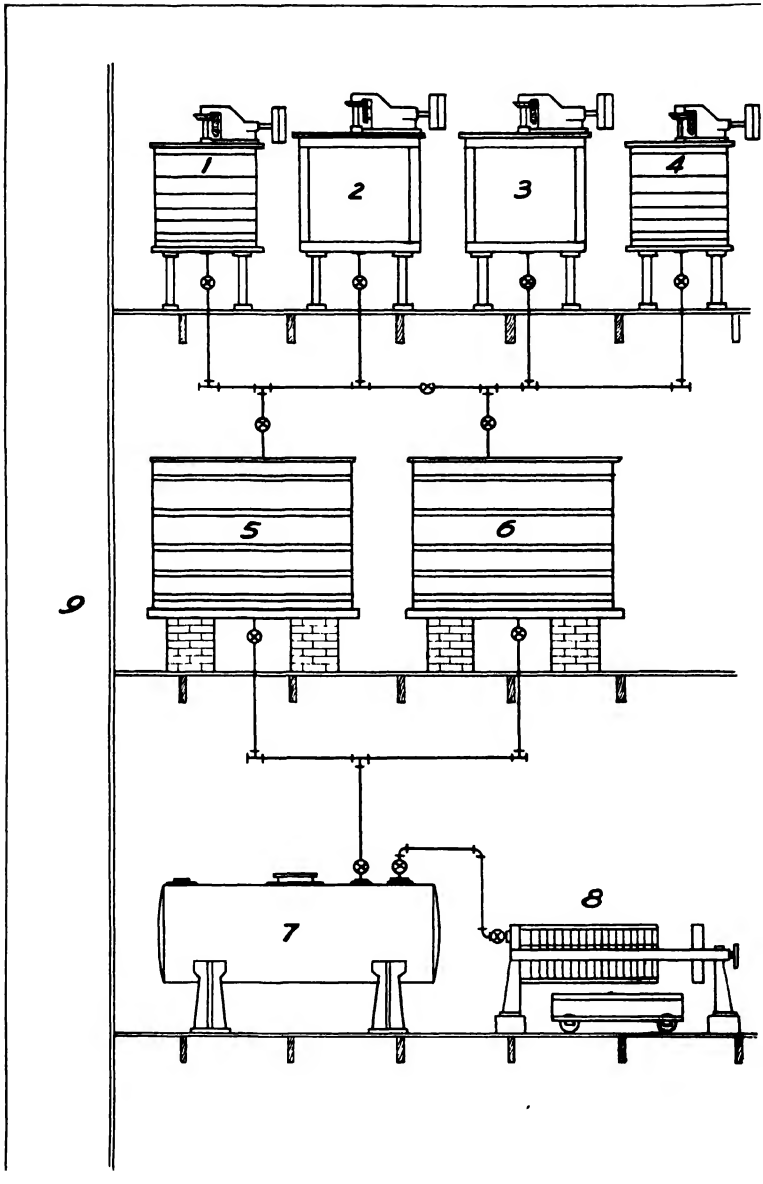


FIG. 26.
Azo Dye Plant. Arrangement of equipment:
1, 4, wooden tubs; 2, 3, iron kettles; 5, 6, large wooden agitated reaction vats; 7, pressure tank; 8, plate and frame filter press; 9, elevator shaft.

two upper stories, three being preferred, with elevator service to each floor. On the third floor up are storage tanks for hydrochloric acid and bins for other raw ingredients. On the second floor are four or more agitated kettles. Two of these are made of wood for preparing the diazotized components of dyes, the other two of iron being for soda liquor of the proper strength and for the solution of metaphenylenediamine, etc. The materials from these tanks which may be of any suitable size are run below into one of two very large agitated vats (3,700 gal. capacity). In these vats the reaction is carried on. The finished dye is run into a blowcase on the ground floor and then filter pressed.

As several days are consumed for the completion of each batch, operations are arranged to start a new charge each day.

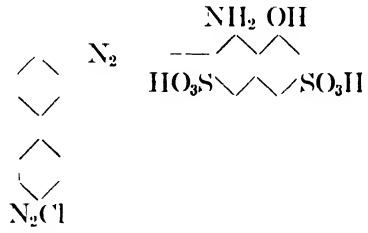
Plant Process—First Day:

Benzidine H acid Intermediate.—The benzidine hydrochloride is ready for diazotization in the large coupling vat 3,700 gal. capacity. (This hydrochloride has been prepared in one of the upper small tanks. The tank which is about half full of water containing 472 lbs. of 30 percent hydrochloric acid is heated up to 70–80°. To this 150 lbs of benzidine are added, and the mixture agitated for half an hour after which it is run down into the coupling vat below and stirred and cooled overnight to 30–40°.) Add 3,000 lbs of ice (10 cakes) to the hydrochloride so that the temperature of diazotization ranges from 0 to 3° at the start to 6–7° at the end. It will be observed that the hydrochloride separates out during the cooling. Now add 113 lbs. of 100 percent $NaNO_2$ or its equivalent of technical product. The bulk of the sodium nitrite is added in crystalline form, about 8–10 lbs. being reserved in solution in a pail, for final adjustment to finish the diazotization. An excess is to be avoided as such will later diazotize H acid, which is evidenced by the formation of a yellow ring on test paper when the H acid is first started in. A faint starch iodide reaction which stays for five minutes indicates the end point.

In the meantime the H acid solution is prepared as follows, so that it will be ready to run into the tetrazo-benzidine. 263 lbs. of 100 percent or 320 lbs. of 84 percent material have been put into an upper wooden vat, the preceding afternoon, and stirred overnight with water at 40° C. 37 lbs. of caustic are dissolved and added so that the solution is faintly alkaline, the temperature being maintained at 30 to 35° C. This H acid solution is run very slowly now into the tetrazo-benzidine solution, about two hours being consumed for the addition. The temperature which is kept at 7° C. during the coupling is permitted to rise to 14° C., as it should be at least 12° C., otherwise a part of the H acid does not react and gives rise to difficulties later on. Care should be taken that the mineral acid reaction of HCl should never disappear. The coupling is finished from a bucket of H acid which has been reserved, the excess of the acid should be only very slight. It is tested with Diazo P.N.A. solution for red violet color, the tetrazo-benzidine being tested with R salt.

The vat is now about half full and should give a faint but distinct acid reaction to Congo. The mixture of the first intermediate which separates out as a fine powdery precipitate is stirred overnight. It is remarkably stable; a cake of ice may be added if desired.

The formula for this first intermediate compound is



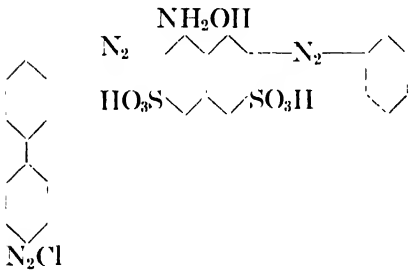
Operations—Second Day:

The formation of the second intermediate Benzidine-azo-H acid-azo-aniline is brought about by diazotizing 77 lbs. of aniline and adding it to the first intermediate at 5° C. Ice is added to take up the heat of reaction. To the aniline being prepard for

diazotization is added 35 gallons of warm water and 260 lbs. of 30 percent HCl. The solution is cooled to 40° and sufficient ice is then added to bring the temperature down to zero, leaving an excess of ice. The solid sodium nitrite (65 lbs.) is then added with constant agitation, finishing as usual with a small amount held reserved. The diazotization is complete when a drop of the mixture reacts with potassium iodide starch paper to give a distinct blue coloration.

After the diazoaniline solution has been all run into the lower vat a prepared cold soda solution (consisting of 385 lbs. of soda ash dissolved in water with steam and stirred cold overnight) is added. Everything will go into solution very rapidly and then in a short while the crystalline second intermediate will separate out completely. If an excess of soda is used, or if the soda solution is added before the diazonum solution, the H acid in alkaline solution will couple on the napthol side with the free remaining diazobenzidine. During this coupling the temperature must be below 7° C. and above 5° C.

To this second intermediate at 50°



(which should show an excess of diazoaniline by giving a distinct reaction with R salt after two hours' agitation)

are added 700 lbs. of salt and a solution of 10 lbs. metaphenylenediamine from one of the upper iron tanks, until a distinct excess is apparent; the latter couples up rapidly to the diazo compound. Some of the coloring matter formed will always go into solution. The solution, which is alkaline, is treated with diluted sulphuric acid and agitated. It should give a faint alkaline final end point. The blue-black crystals, after the addition of the phenylenediamine, turn quickly to gray-black and after a

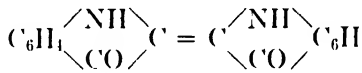
final agitation for two hours the charge is dropped to a blow-case on the ground floor. With air it is transferred to the filter press.

The following day the dye paste is dropped on to small cars and carried to a horizontal vacuum dryer and dried at 100° C. Six percent of sodium carbonate by weight is added and the mass finely disintegrated. The carbonate insures the dye properly going on to cotton.

When m-toluylene diamine is used instead of m. phenylene diamine deep black V is obtained. This possesses a somewhat more reddish shade.

The yield is about 85 percent or 370 lbs. on the ingredients as used.

INDIGO



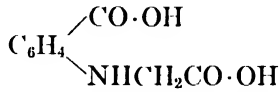
The following brief account of the manufacture of indigo from phenlyglycine treats the subject only as it fits into the outlines of this work as a treatise on "Aniline and Its Derivatives." * The history of indigo production reads like a novel. It is a record of achievement upon achievement, as competitive chemical organizations vied with one another in an effort to discover the more efficient method of production.

The process elaborated here is the method discovered by Heuman and brought to a commercial superiority largely as a result of improvements, both in the preparation of phenylglycine and in its ultimate fusion to indoxyl, which were developed by Farbwerke vorm. Meister Lucius & Brüning.

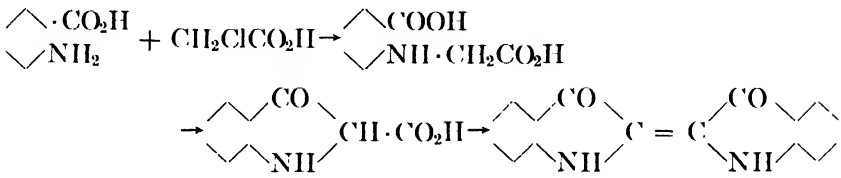
In Heuman's original method, the phenylglycine was converted into indoxyl by fusing with potassium hydroxide at 300°-350°. Owing to these high fusion temperatures and the destructive action of the water liberated during the condensation, the yield was very poor. As a result of this, anthranilic acid was then used as a starting point in the synthesis by

* See Thorpe & Ingold, Vat Colors, for comprehensive review of the subject.

the Badische Co., to form the phenylglycine-o-carboxylic acid.



From this point the condensation to indoxyl is quite similar.



By using sodamide instead of caustic potash, much better results from Heuman's process are, however, obtained since

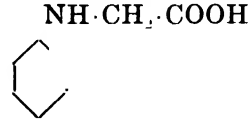
I. The material is a more active condensing agent;

II. It has a low melting point, viz: 155° as compared to 318° for NaOH and

III. It reacts with the water formed, yielding sodium hydroxide and ammonia, thus making possible fusions at 200° C. or lower. In fact, it is necessary to dilute the sodamide with other less active materials, such as a mixture of sodium and potassium hydroxides or sodium cyanides. Owing to the reaction between sodamide and the water liberated, ammonia is continually evolved which is recovered for further use in the preparation of sodamide.

As shown in the diagram below, the first step in the conversion of aniline to indigo is the preparation of phenylglycine. This when condensed with sodamide forms a tautomeric form of indoxyl, two molecules of the latter being then easily oxidized in slightly alkaline solutions to indigo by blowing in air.

PHENYLGLYCINE



Production:

No definite figures are available for the total production of

this important intermediate, which is used as the basis for the manufacturing of indigo. From the production table given below for indigo it can easily be seen that its preparation, if it is all made by the process described, requires more aniline than is used in the manufacture of any one other chemical.

Indigo Production (20 percent paste):

Year	Lbs. Made	Price
1919	8,863,824	$0.59
1920	18,178,231	0.74
1921	6,673,968	0.45
1922	15,850,752	
Total	49,566,775	
Average Production	12,391,699	

Approximately aniline consumed annually, 5,000,000 lbs.

Phenylglycine is prepared by the action of monochloracetic acid on aniline. Owing to its importance as the starting point for the synthesis of indigo and to the difficulty in overcoming the formation of dyglycine, $C_6H_5N(CH_2COOH)_2$ a large number of patents for its preparation have been recorded. A brief description of several of these patents will be noted. This literature is given space here as it affords a splendid opportunity of demonstrating the value of constant research in connection with chemical operations. The advances indicated by the letters patent also reveal methods which, if applied to other processes, may greatly improve operating efficiencies and lead to lower operating costs.

Phenylglycine is converted into (the tautomeric form of) indoxyl by fusion with sodamide. The fusion is performed in large low-pressure autoclaves at 200° C. 40 parts caustic soda, 60 parts caustic potash and 11 parts of metallic sodium are melted and treated with anhydrous ammonia until no further absorption takes place. The ammonia gas atmosphere is maintained on the reaction kettle while 42 parts of the phenylglycine potassium salt are added. Then the temperature of the autoclave is raised to 200° C. and agitation maintained until no further evolution of ammonia occurs.

Two molecules of indoxyl are then oxidized in alkaline solution into indigo.

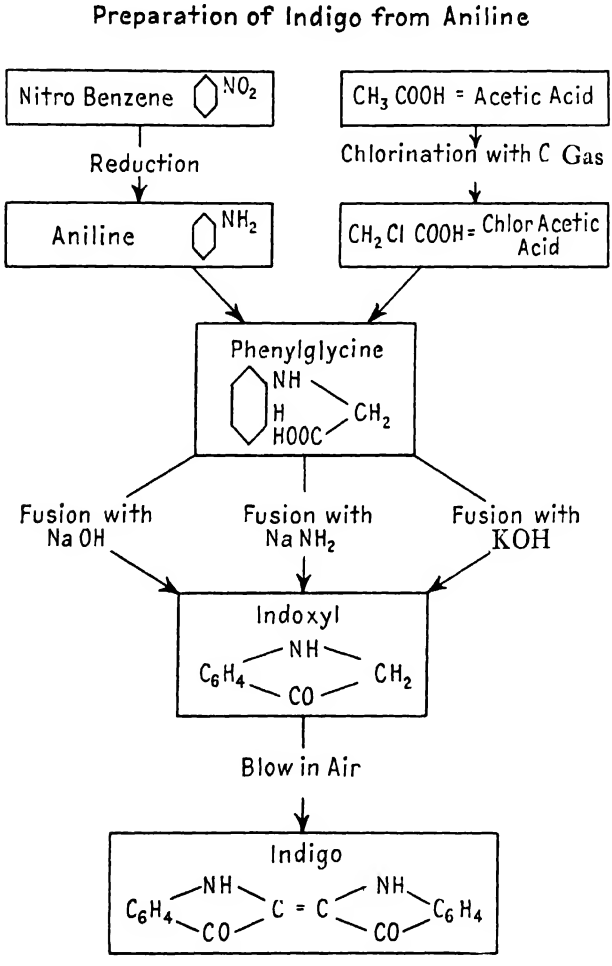
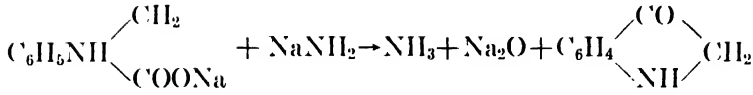
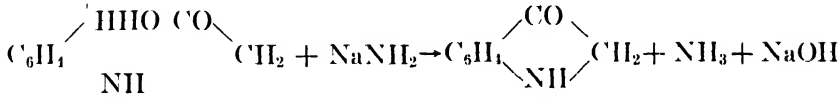


FIG. 27.
Flow Sheet. Indigo Preparation.

Phenylglycine
fusion with
Sodamide
↓

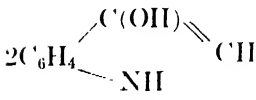


or



Oxidation
2 molecules
indoxyl to
indigo.
↓

or



The ultimate oxidation of the indoxyl is effected by means of a current of air. The indigo separates out in small crystals. The paste after filtration is washed with water, it being then identical with natural indigo. In fact it is superior, owing to its constant composition and higher purity.

Reaction:

$$C_6H_5NH_2 + CH_2ClCOOH \rightarrow C_6H_5NHCH_2CO_2H + HCl$$

Preparation:

The basic method for the production of phenylglycine involves the interaction of an excess of aniline with monochlor-

acetic acid. The reaction mixture is made alkaline and the excess of aniline is then distilled off with steam. The anilid, which is always formed during this reaction, is filtered off. The phenylglycine is then set free and precipitated by means of acid. This involves a separate treatment of the aniline and in view of the fact that the phenylglycine is soluble to a considerable extent in water, the solution after the phenylglycine is precipitated must be evaporated or extracted to obtain satisfactory yields. In order to obtain the best results from this basic reaction, several patents have been allowed.

Process of Badische Aniline and Soda Fabrik,
U. S. Patent 818,341, April, 1906

"Phenylglycine can be prepared more easily with better yields by converting the phenylglycine first formed into anilid, separating this and saponifying it. The operation is carried out preferably in vacuo, the reaction mixture being heated until water ceases to be given off. The mixture is then made alkaline, the excess of aniline distilled off with steam, and the residual liquid allowed to cool, whereupon the anilid which is practically insoluble in cold water is filtered off and washed, and can thus be obtained free from inorganic impurities. The anilid can be completely saponified by heating with a solution of one molecular proportion of caustic alkali, so that by evaporating such a solution the pure phenylglycine salt can be obtained.

"For example, heat together for three hours at a temperature of 100° C. 1 part of chloracetic acid and 5 parts of aniline. Then raise the temperature to 120° C. and continue heating in vacuo at this temperature until water ceases coming over. Sodium carbonate is now added so that the excess of aniline is set free and can be steam distilled. On cooling, the phenylglycine anilid solidifies to a crystalline mass. Filter this off, wash with water, transfer to an agitated autoclave and heat with a solution of one molecular proportion of caustic alkali. When the saponification is complete, distill off the aniline which has

been split off, and evaporate to dryness in vacuo the resulting solution.

"The reaction mixture may be refluxed (as is done in the preparation of acetanilid) by boiling 1 part chloracetic, 2 parts water, 5 parts aniline. When the water is all off caustic soda is added, the aniline layer containing the anilid is separated and one molecular proportion of caustic solution added to it in an agitated autoclave. It is saponified at 140° and the excess of aniline distilled off. The sodium salt of phenylglycine which remains is then evaporated to dryness."

Process of Chemische Fabrik Griesheim Elektron, U. S. Patent 1,011,500

The patentees claim that it is not necessary to form the anilid and go through the troublesome after-separation.

The addition of one equivalent proportion of a neutralizing agent like alkali hydroxid or calcium oxide, added to one of chloracetic acid reacting with three or more proportions of aniline in the melt, combines with the hydrochloride of aniline which is formed during the reaction according to the chemical equation.

$$Cl \cdot CH_2 \cdot COOH + 3C_6H_5NH_2 \rightarrow C_6H_5NH_2HCl + C_6H_5NH \cdot CH_2 \cdot COOH \cdot C_6H_5NH_2$$

This neutralizing agent does not act upon the aniline salt of phenylaminoacetic acid being formed in the process at the same time, and does not transform it into the alkali salt of phenylaminoacetic acid. Owing to this smooth reaction it is possible to obtain from the melt phenylglycine (in form of aniline salt), phenylglycine anilid, and hydrochloride free of alkali chloride.

NOTE: With the introduction of cheaper methods of producing hydroxyethylaniline the following process is likely to prove a serious competitor. Fuse hydroxyethylaniline (137 parts) with potassium hydroxide (500 parts) for one hour at 280–290° C. The indigo is isolated by lixiviation and atmospheric oxygen as before.

D. R. P. 171,172 A. P. 172,775

The aniline set free from hydrochloride by means of alkali acts as a solvent for the phenylglycineaniline salt and anilid. This oily mixture is separated from the alkali chloride and obtained free of it with only small traces of phenylglycine alkali remaining behind. The separated oily mixture may now be transformed into a salt of phenylglycine by heating it up to 130° C. under pressure with the calculated amount of concentrated caustic alkali lye. The aniline is steam distilled from the alkaline solution, and the phenylglycine salt obtained in pure condition with a good yield.

Example: To a hot melt obtained from 500 parts of aniline and 100 parts of chloracetic acid at 150 C., containing about 52 parts of phenylglycineaniline salt and 164 parts of anilid, are poured while stirring 350 parts of slaked lime containing 29.6 parts calcium oxide. As soon as the reaction of the calcium hydroxide upon the hydrochloride of aniline is completed, the oil formed is separated from the hot aqueous calcium chloride solution and directly transformed into phenylglycine potassium by means of 110 parts of a solution containing 50 percent caustic potash. Other alkali or alkali earth compounds may be used, and the methods of combining the constituents rearranged for convenience.

*Processes Farbwerke Meister Lucius Brüning,**
U. S. Patent 868,294

It is found that if phenylglycine and its homologues are separated from the melt formed by the reaction of primary amines with chloracetic acid as the insoluble salts of heavy metals, better yields will be obtained.

Example: 2,500 lbs. of ferrous chloride are dissolved in water and precipitated with the requisite quantity of soda lye or sodium carbonate, whereupon 600 lbs. of common salt are

* This process has been adopted quite generally with only slight modifications in technique, and from every indication appears to be the most satisfactory method yet developed.

added and the mixture heated from 90°–100° C. Now add 944 lbs. of chloracetic acid and stir while 1,020 lbs. of aniline are being rapidly introduced. The charge is now heated under a reflux condenser for one and one-half hours. Upon cooling the phenylglycine iron salt thus obtained is filtered and washed with cold water. The mass is dropped into a kettle stirred with water and decomposed with either soda lye or sodium bicarbonate. The unchanged aniline is steam distilled. The ferrous oxide or carbonate is filtered off, and the phenylglycine is precipitated from the filtrate by carefully adding dilute mineral acid.

A deviation of the reaction above previously made public by the same company uses nitrobenzene and iron with chloracetic acid to form phenylglycine. The comparative insolubility of the heavy metal salts of phenylglycine were here found to prevail and led to the use of this discovery in the process described above. 620 lbs. of nitrobenzene, 1,000 lbs. of iron borings and 70 lbs. of aniline are heated in an aniline reducer to 70°, 470 lbs. of monochloracetic acid dissolved in water are now added. The temperature of the chloracetic charge is raised to 90° C. and the reducer kept refluxing during the addition.

The heating of the charge is continued for several hours after which it is neutralized with soda ash. The aniline is steam distilled and again used in ensuing runs. The reducer charge is filter pressed and washed thoroughly with hot water. The solution may be concentrated before separating the phenylglycine with the requisite quantity of mineral acid.

Process of Chemische Fabrick Weiler Ter Meer,

German Patent 244,825

Four parts of aniline are refluxed in a reducer at 90°–95° and an aqueous solution containing two parts of chloracetic acid is run in. The calculated amount of a neutralizing agent, *e.g.*, alkali hydroxides or carbonates in solution, is run in simultaneously and independently so that the reaction mixture is just

about neutral at all times. The charge is refluxed until the reaction is complete, after which it is cooled and the crystalline aniline salt of phenylglycine separated out. This can be filtered, washed, and subsequently treated with alkali to liberate the aniline. The phenylglycine is then precipitated with mineral acid.

Phenylglycine may also be obtained economically using Bucherer's process * by condensing aniline and formaldehyde. The bisulphite compound of formaldehyde is first condensed with aniline

$$C_6H_5NH \left| \begin{matrix} H \\ \\ \end{matrix} \right. \quad \left. \begin{matrix} HO \\ \\ \end{matrix} \right| - C \begin{matrix} H \\ - \\ H \end{matrix} SO_3Na \rightarrow C_6H_5NHCH_2 - SO_3Na$$

This product is then treated with sodium cyanide

$$C_6H_5NHCH_2 - SO_3Na + NaCN \rightarrow C_6H_5NHCH_2CN + Na_2SO_3$$

The nitrile thus obtained on saponification yields phenylglycine

$$C_6H_5NHCH_2 - CN + 2H_2O \rightarrow C_6H_5NHCH_2 \cdot COOH + NH_3$$

The following dyestuffs of the Indigo Group are prepared from phenylglycine: Indigo, Indigo MLB, Indigotine, Indigotine P, Brom Indigo, Helindone Blue BB, Dianthrene Blue 2B, Indigo MLB/5B, Brilliant Indigo BASF/2B, Brilliant Indigo BASF/B, Indigo Yellow 3G, Ciba Yellow G.

The Preparation of Indigo

The finished phenylglycine after being dried and finely ground is converted first to indoxyl and subsequently oxidation to indigo. The phenylglycine is converted to indoxyl by fusion at 200° C. with sodamide and caustic soda.

The following is a brief description of the process:

The sodamide pot is gently heated until it is absolutely dry, after which the required amount of metallic sodium is introduced in brick form, through a large flanged opening. The pot is sealed and then heated by gas or oil, until the mass is fused. The fusion temperature is maintained while anhydrous ammonia

* D.R.P. 157,710—157,909—158,090—158,346—169,186—181,723.

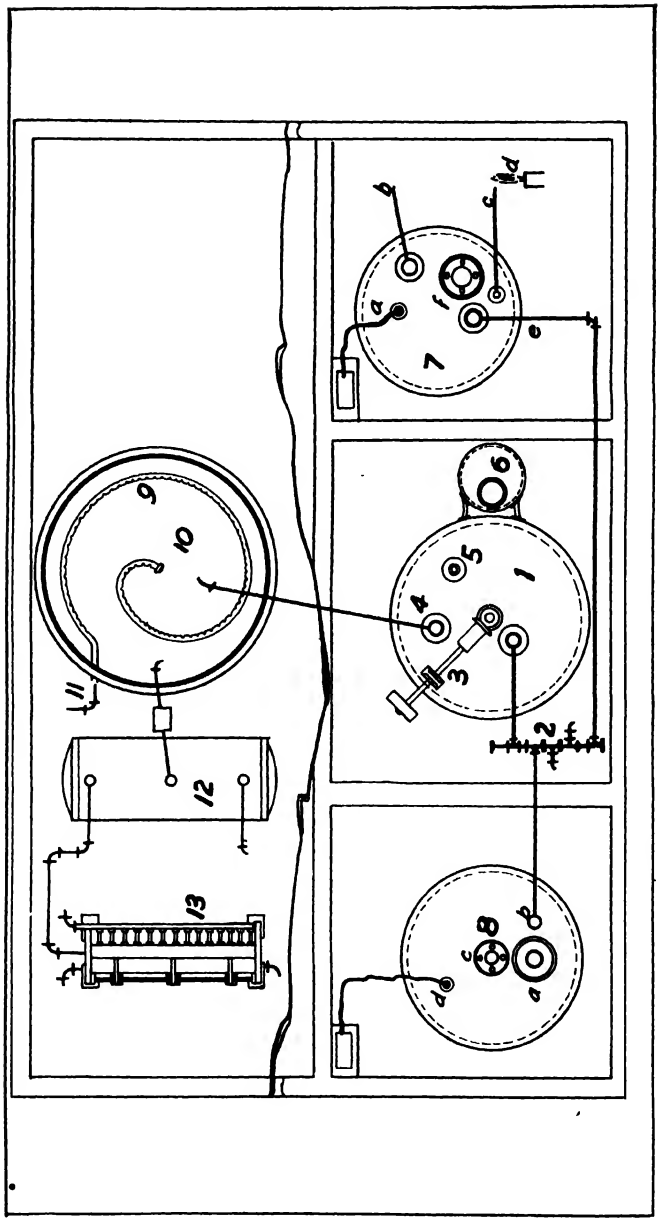


FIG. 28. Indigo Plant. Arrangement of equipment:

1, C-1 autoclave; 2, distributor; 3, agitator shaft and gears; 4, blowleg to oxidation tank; 5, pressure and temperature recorder; 6, phenylglycine hopper; 7, sodamide kettle: *a*, thermometer coupling; *b*, ammonia gas inlet; *c*, hydrogen gas outlet; *d*, hydrogen burner; *e*, delivery line to autoclace; *f*, manhole for introducing metallic sodium; 8, caustic fusion kettle: *a*, manhole, *b*, delivery line to autoclave; *c*, agitator; *d*, thermometer couple; 9, nickel perforated air distributor; 10, oxidation vat; 11, outlet connection to 12, pressure kettle; 13, pressure filter press.

is slowly fed into the mass from a cylinder. The hydrogen formed is led to a pilot light and burned off at the outlet. The reaction is almost complete when the hydrogen light fails, the temperature is then raised slightly while the ammonia feed is continued for half an hour until the reaction is completed.

The caustic pot, like the sodamide pot, is adjacent to, but on the opposite side of the reaction autoclave. A large quantity of fused dry caustic is kept ready to feed to the autoclave.

With all vents open the autoclave is heated gently to dryness. The feed lines from the sodamide and the caustic pots are warmed to prevent stoppage during the material transfer. The autoclave is now completely evacuated and the agitator put into motion. The sodamide is first drawn into the autoclave and the feed line drained clear, after which the temperature is raised to that of the caustic dehydrating pot and the required amount of fused caustic drawn in.

The temperature is raised to 200° C., and the pressure regulated at about 200 lbs. per square inch. The phenylglycine which has been previously dried in a vacuum dryer and ground to a very fine powder is now fed into the autoclave. The powder is put into a hopper with a screw feed, which delivers it to a horizontal plunger, discharging into the side of the autoclave. The plunger has a hollowed central section which takes the feed, and the front and back portions making tight joints. The phenylglycine is added very slowly, about one pound of the intermediate being delivered every five minutes for each hundred pounds of indigo estimated. The temperature and pressure are maintained for two hours after the feed is complete.

The discharge line from the autoclave is heated and the oxidizing tank prepared by running in a quantity of water equivalent to five times the volume of the autoclave charge. The discharge valves from the autoclave are opened and the batch is delivered to the bottom of the oxidizing vat. Air is blown through a perforated oxidizing coil for several hours until the charge is ready for filtration.

The charge is dropped into a blowcase by gravity and sub-

sequently filtered through a pressure filter press. The cake is washed with cold water to faint alkalinity.

In plants where the sodamide pot is eliminated the practice is similar to that previously outlined at the beginning of this chapter. The autoclave is opened and dried and the metallic sodium introduced through a manhole. The manhole is replaced and the autoclave temperature brought up to the fusion point whereupon the anhydrous ammonia is introduced at the base of the machine. The hydrogen is burned off as usual. The caustic is now drawn in, followed by the addition of the phenylglycine. At one Continental plant the introduction of both the caustic soda and metallic sodium to the dry autoclave, before adding the ammonia to the fusion mass to form the sodamide, has been under consideration.

Aniline in the Rubber Industry

According to estimates submitted by the producers, about 20 percent of the total American aniline production is utilized in the rubber industry. It is now seldom used in its pure state, as an accelerator, owing to the fact that in the past several cases of severe aniline poisoning had developed. Lately, however, a large number of products derived from aniline oil have found favor.

Accelerators are used in the rubber industry to cut down the vulcanization period without modifying greatly other factors contributing to this reaction, viz.: raising the temperature or increasing sulphur ratio. Thus by introducing into the rubber batch certain organic substances the reaction is expedited. This fact was established when efforts were made to vulcanize acetone-extracted rubber or synthetic rubber. In both cases vulcanizing was not satisfactorily accomplished. An examination of the acetone extract revealed certain nitrogenous bodies, and the introduction of these into the caoutchouc (synthetic rubber) shortened the time of reaction. Based upon this finding it was believed that the nitrogen molecule in certain organic intermediates had a definite action in expediting

the vulcanization and curing of the rubber batch. As a result of this discovery investigations are now being directed toward the perfection and production of accelerating substances, and also into the technique of their use.

"In a more recent theory * to explain the action of certain organic substances it is said that the acceleration of vulcanization of rubber depends largely on the action of H_2S forming polysulfides of sulphur, the sulphur of which is readily available (comparable to nascent gases) for vulcanization. The organic accelerators may be divided into two classes:

"(1) H_2S polysulfide accelerators, whose bases form polysulfides similar to yellow ammonium sulfide.

"(2) Carbosulphydril polysulfide accelerators containing the group C·SH including the thioureas, dithiocarbamates, etc. In the first class the sulphur is related to the sulphydril group attached to the nitrogen molecule, while in the second class it is linked to the carbon molecule. Phenylated guanidines belong to both classes; since at curing temperatures they easily react with H_2S to form thioureas and free amines. Diphenylguanidine, for example, yields thiocarbanilide and ammonia.

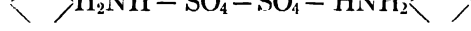
"It is known that sulphur reacts with rubber and proteins at 140° C. to form H_2S. This in the presence of hydrosulfides, which in turn take up sulphur to form basic accelerators, forms polysulfides. These impart their sulphur in a more active form to the rubber batch, producing vulcanization."

Aniline oil has been used directly as an accelerator by simply pouring the oil into the rubber compound when it has broken down on the hot mills. It hastens the cure of rubber articles, and makes vulcanization possible in a shorter time, with the addition of less sulphur, thereby minimizing to a great extent flaws in the finished product. But as previously noted the use of pure aniline has resulted in many cases of aniline poisoning and consequently derivatives of this important intermediate, the effects of which are less harmful, have been brought into use. The more noteworthy of these (which are elaborated

* Theory of Vulcanization: Scott & Bedford, J. I. and E. C., 13, 125, 1921.

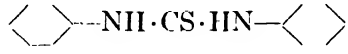
upon here) are Aniline Sulphate, Thiocarbanilide, Paraphenylenediamine, Paranitrosodimethylaniline, Quinoline, Formanilid, Diphenylguanidine and Triphenylguanidine.

ANILINE SULPHATE



The use of aniline sulphate as an accelerator is increasing rapidly, approximately 200,000 lbs. being used during the year 1922. Its preparation is similar to that of aniline hydrochloride.

THIOCARBANILIDE



Production:

Year	Lbs Made	Price
1918	1,326,236	$0.47
1919	2,268,375	0.35
1920	2,226,807	
1921	1,185,462	0.42
1922	2,591,856	0.27
Average Production	1,919,747	

Average annual production—1,751,720 lbs.

Aniline consumed in manufacture—1,500,000 lbs.

Process Involved: Condensation—aniline with carbon bisulphide.

Reaction:

$$2CS_2 + 2C_6H_5NH_2 \rightarrow C{=}S \begin{matrix} C_6H_5NH \\ C_6H_5NH \end{matrix} + H_2S$$

Preparation:

Thiocarbonilide was one of the first of the aniline derivatives to be used as an accelerator, and it still finds widespread appreciation in the rubber industry. It is made by bringing aniline and carbon bisulphide together in the presence of alcohol or sodium polysulphide. The apparatus used is usually a standard, jacketed, iron reducer, provided with a reflux condenser.

One thousand pounds of aniline and an equal amount of carbon bisulphide are run into the kettle. Seven hundred fifty pounds of 95 percent alcohol are added before the machine is closed for heating. The batch is then boiled and refluxed for ten to twelve hours by maintaining a steady heat at the boiling point which is slightly over 46° C. The reaction starts immediately with the evolution of H_2S, which is liberated to the outside from the top of the reflux system. The thiocarbonilide will start precipitating out in the form of white crystalline plates, after the reaction has been carried on for several hours. The completion of the reaction is determined by testing a sample from the kettle, which should, after distilling off the CS_2 and alcohol, show no traces of free aniline, when washed with water and HCl.

When the tests show that the batch has been converted, the carbon bisulphide and alcohol are distilled off. The distillate is analyzed by fractional distillation, and more CS_2 is added to recharge the recovered material, so that it conforms to the standard charging mixture, and can again be used.

Having distilled off the carbon bisulphide and alcohol, water is now run into the kettle. The charge is agitated to stir up the crystals and it is thus possible to obtain a very satisfactory washing of the product. The water thins the charge down to a point where it can run on to a centrifuge or filter press. The cake should be free from all traces of aniline. If it is desirable the temperature of the charge (after the alcohol and carbon bisulphide are distilled off) can be raised to 160° C. which is above the fusion point of the mass, and the charge then run out into crystallizing pans to cool.

The yield by the above method is almost theoretical.

A variation of this process is to use sodium polysulphide in the charge, instead of alcohol, along with the combining elements. 1,000 lbs. aniline and 1,100 lbs. of carbon bisulphide are put into the reaction kettle and a small quantity of sodium polysulphide is added. Heat is applied and the charge refluxed

under a slight pressure for thirty hours. The excess of carbon bisulphide is steamed off at the close of the cooking period.

When pure materials are used no purification of the thiocarbanilide is necessary. When the product is fused it comes out in the form of a hard, yellow, crystalline cake. It should have a melting point of 154° C. The yields are about 123.6 lbs. thiocarbanilide per 100 lbs. of aniline used.

From thiocarbanilide are derived a large number of dyes belonging to the Indigo Group.

Before using as an accelerator, the crystals or cake must be removed from the pan and be pulverized. Care should be taken to reduce it to a very fine powder as it has a tendency to flake. Failure to reduce it to a fine state of subdivision will produce hard kernels of overcured rubber through the product. As an accelerator it is used in amounts from one-half to two percent of the batch weight.

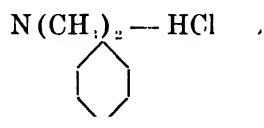
Thiocarbanilide of itself exerts practically no accelerating influence (according to the annual report 1920 British Institute) but in the presence of 1 percent zinc oxide a very appreciable acceleration is produced. Some investigators advise the use of iodine or pyridine in the batch to facilitate the evolution of H_2S during the cooking period.

P. PHENYLENEDIAMINE

This dyestuff has been used extensively as a rapid accelerator. Lately, its use has been curtailed owing to cost consideration. Its preparation from p. nitroaniline by reduction with iron borings and hydrochloric acid is described after p. nitroaniline manufacture.

PARANITROSODIMETHYLANILINE

HCl-salt →



Production	Lbs. Made	Price
1918	851,821	$0.53
1919	592,663	0.61
1920	155,986	0.99
1921	104,690	1.56
1922	94,831	

The hydrochloric acid salt of p. nitrosodimethylaniline has been put on the market as an accelerator under the trade name of accelerene.

Manufacture:

The reaction vat is prepared by introducing a small quantity of water and 1,000 pounds of ice. Agitation is started and 950 pounds (8 carboys) of 32 percent HCl are added. 400 pounds of dimethylaniline are now very slowly fed in. Ice is added if necessary to bring the temperature back to 0° C.

In a small tank 250 pounds of $NaNO_2$ are mixed with just enough water to dissolve and this solution of nitrite is then run very slowly into the large reaction tank, introducing it under the surface of the liquor. This operation should consume about eight hours. By means of necessary additions of ice the temperature is controlled at 0° C., about 2,200 pounds being required for each batch.

When diazolization appears complete as evidenced by the odor of free nitrous acid (as it is not possible to spot for free nitrous acid with starch iodide paper, the p. nitrosodimethylaniline itself reacting with it), a slight excess of $NaNO_2$ is added and the stirring continued for a short time. The batch is then run into a filter box.

The valves to the reaction tank are closed and about 1,000 pounds of water run in. The agitator is started and 200 pounds of salt are introduced. The batch in the filter box has now been drained until most of the liquor has filtered off. The salt solution from the reaction tank is now used to wash the precipitate in the filter box by running it over the cake.

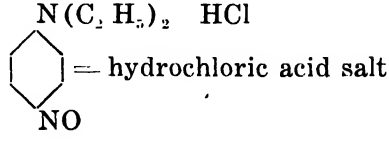
The precipitate is then centrifuged and finally spread upon trays to dry. P. nitrosodimethylaniline cannot be dried satisfactorily in anything but an air dryer at 30° C.

The yield is 580 pounds or about 94 percent of theory.

It usually comes on the market as hydrochloride which melts at 177°; the base melts at 92°. The hydrochloride, in addition to being used in the rubber industry, is used for making:

Indophenol	Indolizarine Green
Capri Blue	Modern Violet
Pyrogallol-Cyanine	Prune
Sulfonic Acids	Gallamine Blue
Modern Violet N	Amido Gallamine Blue
Gallocyanine	Gallanilic Violet RB
Modern Cyanine	Modern Azurine DH
Gallocyanine MS	Phenocyanine TC
Gallogreen DH	Phenocyanine TV
Cyanazurine	Ultracyanine B
Chromocyanine V	Gallazine A
Ultra Violet LGP	Nitroso Blue MR
New Blue R	Fast Neutral Violet B
New Blue B	Methylene Gray O
New Methylene Blue GG	Nigramine
New Fast Blue F	Rhoduline Violet
Muscarine	Tannin Heliotrope
Fast Black	Indazine M
Methylene Blue	Metaphenylene Blue B
Methylene Green O	Napthazine Blue
Thionine Blue GO	Rubramine
Neutral Red	Indamine 3R
Neutral Blue R	Indamine 6R
Immedial Sky Blue	

PARANITROSODIETHYLANILINE



Preparation:

This is made in a manner similar to that described above for paranitrosodimethylaniline. Several modifications in tech-

nique have to be made in consequence of the high solubility of paranitrosodiethylaniline hydrochloride. This brine is used in the jacket of the kettle to produce refrigeration to the temperature required for nitrosation, *i.e.*, —5°, and concentrated hydrochloric acid is used for the reaction. The operation is carried out in an enamel-lined kettle.

P. nitroso-diethyl-aniline is used also in the preparation of Gallanilic violet RB, coreine RR, coreine AR.

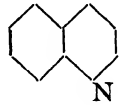
QUINOLINE

Quinoline and its derivatives are also used quite satisfactorily as accelerators.

Reaction:

$$C_6H_5NH_2 + C_3H_5(OH)_3 + O = C_9H_7N + 4H_2O$$

The graphic formula shows that it exhibits to napthalene the same relation that pyridene bears to benzene.



Manufacture:

Skraup's synthesis for quinoline as outlined by Perkin and Kipping can be utilized for the preparation of quinoline, as follows: A mixture of 38 parts of aniline, 24 parts nitrobenzene, and 120 parts glycerine are put in a jacketed, agitated kettle provided with refluxing apparatus (aniline reducer can be used). To this mixture 100 parts of concentrated sulphuric acid are gradually added. The batch is then carefully heated by superheated steam or oil, through the jacket. A rather violent reaction will set in at the start so that effective cooling by the condensers will be required. When the reaction subsides the boiling is continued for four hours. The charge is then cooled and diluted with water.

Live steam is now admitted into the still through projected steam pipes or, in the case of some reducers, through the shaft,

and the nitrobenzene is distilled out, the condenser liquid being now led to the nitrobenzene container, instead of refluxing back to the still. When samples taken at the base of the condenser show that all the nitrobenzene is distilled out an excess of soda is added to liberate the quinoline and the unchanged aniline

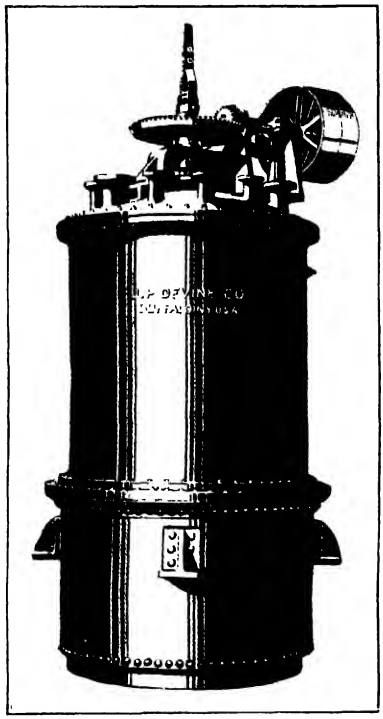


FIG. 29.
Reducer (Jacketed).
Equipped with device for raising stirrer from charge in kettle. (Devine Manufacture.)

from their sulphates. The mixture is then again distilled into a second reduction kettle. As these two bases cannot be well separated by fractional distillation, the whole of the aqueous distillate is then acidified with sulphuric acid, and sodium nitrite added until nitrous acid shows on testing with starch iodide paper, after thorough agitation. The charge is then heated

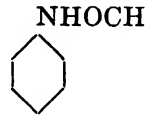
through its jacket until the diazo salt is converted into phenol. It is now made alkaline with soda and again steam distilled. The distillate is now led to a conical-bottom receiver, where it is separated from its aqueous solution.

This crude quinoline base has to be purified by fractional distillation. As it is not easily handled it is usually converted into its sulphate and most frequently used thus.

Quinoline is an oily liquid boiling at 238° C. Its specific gravity at 20° C. is 1.094.

It is also used extensively in the manufacture of quinoline red, quinoline blue and quinoline yellow.

FORMANILIDE



This derivative, according to the " Census of Dyes, U.S.Tariff Commission," is gaining widespread popularity as an accelerator.

This is the anilide of formic acid, and is prepared by heating the aniline salt of formic acid. The technique is similar to that described under acetanilid in the manufacture of paranitroaniline.

DIPHENYLGUANIDINE, TRIPHENYLGUANIDINE

Phenylated guanidines from their structures appear to be destined to play a very important rôle as accelerators. As pointed out by Scott & Bedford,* they belong to both classes of accelerators capable of exercising marked influence in expediting vulcanization.

These substituted guanidines are very closely related to thiocarbanilide in structure and are made from it on a plant scale.

$$\begin{array}{l} S - NH \quad C_6H_5 \\ \| \\ C - NH \quad C_6H_5 \end{array}$$ Thiocarbanilide

* J. I. C., 13, 125, 1921.

$$NH = C \left\langle \begin{matrix} NH_2 \\ NH_2 \end{matrix} \right. \quad \text{Guanidine}$$

By replacing S with an imido radicle

$$NH = C \left\langle \begin{matrix} NH \cdot C_6H_5 \\ NH \cdot C_6H_5 \end{matrix} \right. \quad \text{Diphenylguanidine from Thiocarbanilide}$$

According to the "Census of Dyes," U. S. Tariff Commission, the manufacture and sale of phenylated guanidines has increased tremendously during the past two years.

DIPHENYLGUANIDINE

$$HN = C \left\langle \begin{matrix} NH \cdot C_6H_5 \\ NH \cdot C_6H_5 \end{matrix} \right.$$

$$S = C(C_6H_5NH)_2 + NH_3 \rightarrow HN = C(C_6H_5NH)_2 + H_2S$$

Preparation:

Thiocarbanilide is treated in a steam jacketed kettle with an excess of aqua ammonia 26° to which concentrated KOH has been added. Lead oxide (PbO) is used as a catalyst. The sulphur group is quite easily replaced by NH with the evolution of H_2S. The excess of ammonia is steamed off at the close of the operation and the base which is soluble in cold alcohol is extracted. It crystallizes in monoclinic needles from the alcohol which is recovered for further use. Great care must be taken to have the system tight—for if ammonia is lost during the reflux, the reaction does not progress satisfactorily. To overcome this difficulty salts of ammonia are used, as described in the following process:

Diphenylguanidine is being manufactured successfully also by the following process in which ammonium nitrate replaces aqua ammonia in the reaction mass. The operation is carried on in a standard jacketed reduction kettle which is fitted up with reflux apparatus. A heel of 400 gals. of alcohol is first run into the kettle and to this 760 lbs. of a pure grade thiocarbanilide are slowly added. The purity of the carbanilide has an important bearing on the quality of the finished product as traces of nitrobenzene, aniline, or sulphur in this ingredient

cause darkening of the finished material. About 460 lbs. of ammonium nitrate are then introduced into the kettle under agitation and the batch warmed up to 30° C. in not less than one-half hour. When this point is reached 440 lbs. of litharge are added and the temperature then raised to 85° C. The reaction is quite brisk and the reflux comes over freely. The cooking is continued for a period of one and a half hours at which time the reaction is completed.

The distilling valve is now closed and with a slight pressure on the reaction kettle the charge is filtered through a plate and frame press. The liquor which contains the diphenylguanidine in hot alcoholic solution is led to a copper still which is equipped for the recovery of the alcohol. Here the charge is heated by jacket steam and the alcohol distilled off, condensed, and recovered for further use. When the alcohol is removed, cold water is run into the still and this causes the base to separate out as it is insoluble in an aqueous solution. The charge is now delivered to the press previously used and the cake is washed with warm water at 50° C. This crude diphenylguanidine is removed and put into a vat containing a small quantity (10–40 lbs.) of caustic. The latter exerts a purifying influence by removing tarry impurities and the color of the material should, after agitation in the alkaline solution, be white. The contents of the vat are centrifuged and the base after washing in the wringer is dried and pulverized.

Diphenylguanidine melts at 147°. It is insoluble in cold aqueous solution, but very soluble in alcohol.

TRIPHENYLGUANIDINE

$$C_6H_5N = C \begin{cases} NH \cdot C_6H_5 \\ NH \cdot C_6H_5 \end{cases}$$

Preparation:

Molecular quantities of aniline and thiocarbanilide are added to a hot alchohlic solution in a steam jacketed kettle. A calculated quantity of lead oxide (PbO) based on aniline used is added as catalyst. The charge is heated and refluxed until the reaction is complete, after which it is filter-pressed. The alco-

holic charge containing the base is led to a still where the free alcohol is distilled and recovered. The charge is then run into a tub containing a small heel of cold water. The base separates out and is washed with dilute caustic, it is then filtered and the press cake after removal is then dissolved in alcohol and evaporated to dryness in a vacuum dryer. The alcohol from both steps is recovered for further use.

Triphenylguanidine melts at 145° C. It crystallizes easily in needles and rosettes from hot alcohol. It is almost insoluble in hot aqueous solution.

CHAPTER XV

THE ACTION OF ACIDS AND ALKALIS ON ENGINEERING MATERIALS

Corrosion

The study of corrosion is at present receiving widespread attention, not only among chemical engineers but also by other engineering societies. During recent years, the rapid growth of the chemical industry, accompanied by the discovery of new products, has necessitated the use of a large number of metals and alloys in the manufacture of equipment. Oftentimes a process which has been worked out successfully in the laboratory meets with only an indifferent success in the plant due either to a thoughtless selection of apparatus, or to difficulty in finding suitable engineering materials that will withstand the corrosive action of the chemicals to be handled. Laboratory experiments are usually conducted in glass equipment. Semi-works investigations confirming the preliminary data are ordinarily conducted only for short periods of time, in the most convenient apparatus available, and therefore do not give accurate information as to the durability of the equipment that will be provided for the plant operations.

Information leading to a true estimation of the corrosive action taking place in carrying out operations must, however, be available to the chemical engineer in order that the subsequent performance of chosen equipment will reflect, to a great degree, the assumptions based on preliminary investigations.

Six factors * stand out above others in making the decision. They are

1. Permanence of the process.
2. Long life of equipment or, in other words, cost per unit of unit of time while equipment is in service.
3. Contamination of manufactured product with products of corrosion.

* Harold F. Whitaker. Paper del'd before A. I. C. E. (June, 1923).

4. Replacement cost including replacement repairs, as well as time and profits lost by shut down.
5. Efficiency of machine with respect to the transfer of heat, etc.
6. Intrinsic value of structural materials when the equipment is scrapped.

The importance of the third item—contamination of the finished material with products of corrosion—cannot be overestimated, as an inferior article has not only a limited market at a reduced price, but also often necessitates extraordinary manipulation in the plant, making for lower yields and higher costs.

Very often the introduction of corrosive contamination is due to impurities either in the reagents used or to impurities in the materials of construction. It has been proven in many instances where the best engineering advice has been followed in the choice of equipment that subsequent difficulties due to corrosion were caused by the action of slight impurities present in one or both of the sources just referred to.

The following tables on the action of acids and alkali on engineering materials * are to be used merely as a guide for more exhaustive tests made under conditions simulating plant practice as closely as possible. Such tests should be an integral part of the report emanating from the laboratory covering the process of manufacture, for such information is indeed vital to the ultimate success of any operation.

Aluminum

Acetic Acid ($CH_3CO \cdot OH$)

Aluminum is very slowly soluble in acetic acid, but solubility is increased by presence of sodium chloride (NaCl). It is only slightly acted on by cold acetic acid, and the action is only slightly increased by heating of the acid.

* Prepared by G. N. Harcourt, M. W. Kellogg Co.

Alkalis

Aluminum is quickly covered, in presence of air, with a layer of oxide, which prevents further oxidation of the metal. Aluminum is inconstant with substances which dissolve this layer, such as acids, alkalis, etc.

If moderately concentrated potassium lye is warmed with aluminum, a lively evolution of hydrogen takes place, and the metal is completely dissolved.

Aluminum is very slowly soluble in dilute or concentrated potassium hydroxide (KOH) or sodium hydroxide (NaOH), and is slowly attacked by ammonium hydroxide (NH_4OH); it is soluble in barium hydroxide (BaO_2H_2), and slowly so in calcium hydroxide (CaO_2H_2).

Ammonia (NH_3)

Ammonia attacks aluminum only very slowly.

Hydrochloric Acid (HCl)

Hydrochloric acid attacks aluminum most violently, and dissolves it, whether dilute or concentrated, hot or cold.

Nitric Acid (HNO_3)

Aluminum is not attacked by nitric acid when concentrated and scarcely when boiling; it is, however, insoluble in nitric acid in vacuo. It is so slowly soluble in nitric acid that 100 cc. require two months to dissolve 2 gr. aluminum.

Dilute nitric acid acts slowly on aluminum in the cold, but exerts a fairly vigorous action at the boiling point. The action diminishes as the concentration increases.

The resistance of this metal to corrosion by nitric acid is such that it is stated (Hoppe, Die Chemischen Reaktionen) that dilute or concentrated, hot or cold, nitric acid has no action on *pure* aluminum.

Sulphuric Acid (H_2SO_4)

Dilute sulphuric acid dissolves aluminum very slowly, with evolution of hydrogen, when warm. To cold dilute suphuric

acid aluminum is very resistant, it being almost insoluble. Concentrated sulphuric acid dissolves aluminum slowly on heating, with evolution of sulphur dioxide. This metal is insoluble in dilute sulphuric acid in vacuo, however.

COPPER

Acetic Acid

Copper is more or less soluble in dilute acetic acid when a supply of air is afforded, but absolutely insoluble when air is wholly excluded.

Alkalis

Copper is relatively constant with weak alkali solutions. In concentrated 5 percent–50 percent sodium or potassium lye, in presence of air, perceptible amounts are dissolved, however. An 0.9 percent lye absorbs no copper.

When in contact with air, copper is oxidized by alkalis (especially ammonium hydroxide, NH_4OH). It is soluble in ammonium carbonate ($(NH_4)_2CO_3$).

According to Lunge and Weibel (Ch. Ind., 9, 47), 10–50 percent caustic soda lye dissolves, at 20°, in seven days, up to 0.02 gram copper; at 100°, the same quantity is dissolved in two hours.

Honigman (Dingl., 261, 550) recommends as a protective measure the placing of iron wire in the vessels in which alkali lye is to be evaporated.

Copper is fairly constant with alkalis which are being melted. It is not attacked by ammonium nitrate (NH_4NO_3), potassium nitrate (KNO_3), or ammonium sulphate ($(NH_4)_2SO_4$).

Ammonia

Copper dissolves in ammonia in presence of air; it is disintegrated completely at 400–900°.

Hydrochloric Acid

Copper is but very slowly attacked by cold hydrochloric acid of 1.12 sp. gr., but somewhat more on warming; it is even less soluble in dilute.

It is indifferent to this acid if air is excluded, being fairly constant in the dilute acid in this case.

Nitric Acid

Nitric acid, whether weak or concentrated, acts readily on copper. Molinari (Inorganic Chemistry) states that dilute nitric acid dissolves this metal even in the cold.

With very concentrated nitric acid copper becomes passive. Nitric acid of 1.07 sp. gr., or less, does not attack copper at 20°, but if potassium nitrite (KNO_2) is added the action begins at once. If nitric acid is more concentrated, the copper is attacked. Nitric acid of 1.108 sp. gr. begins to act at — 2°, and of 1.217 sp. gr. at — 10°. Nitric acid of 1.512 sp. gr. attacks copper violently at 20°, but action soon ceases on account of formation of a crust of copper nitrate ($Cu(NO_3)_2$), insoluble in pure nitric acid.

30 percent nitric acid at 30° does not dissolve copper, provided nitrous acid is neither present nor formed subsequently.

The destructive action of nitric acid is lessened to a large extent if the formation of nitrous acid is prevented—by the addition, for instance, of urea, or of oxidizing agents like potassium perchlorate ($KClO_4$) or potassium manganate (K_2MnO_4).

Sulphuric Acid

Boiling sulphuric acid above 130°, when concentrated, dissolves copper. Weak acid does not act energetically unless air is present, when the action is quick. It is indifferent in vacuo.

5–10 percent sulphuric acid does not dissolve copper, and even if air is present the solubility is relatively slight at the ordinary temperature, even after a long time. Hot concentrated sulphuric acid, on the other hand, attacks copper energetically.

According to Comey, sulphuric acid acts but slightly even at 20°.

Pickering (Chem. Soc., 33, 112) states that 16.3 gr. sul-

phuric acid (1.843 sp. gr.) dissolved the following amounts from 3 gr. copper having a surface of 65 sq. cm. at the given temperature:

Temperature	Time	Percent Copper Dissolved
19°	14 days	about 6
60	120 min.	2.5
80	30 "	1.5
100	30 "	3.1
124	30 "	22.7
130	30 "	32.6
137	30 "	35
150	30 "	69.2
170	10 "	51.92
195	2 "	53.5
220	½ "	70.57
270	few seconds	nearly 100

With dilute acid the action was much less violent:

100°	30 min.	H_2SO_4	1.843 sp. gr.	2.380%
100	30 "	$2H_2SO_4$, H_2O	1.8295 " "	0.585%
100	30 "	H_2SO_4, H_2O	1.780 " "	0
100	30 "	H_2SO_4, $2H_2O$	1.620 " "	0
130	30 "	H_2SO_4	1.843 " "	32.6 %
130	30 "	H_2SO_4, H_2O	1.780 " "	1.18 %
130	30 "	H_2SO_4, $2H_2O$	1.620 " "	0
165	15 "	H_2SO_4	1.843 " "	70 %
165	30 "	H_2SO_4, H_2O	1.780 " "	16.5 %
165	30 "	H_2SO_4, $2H_2O$	1.620 " "	2.7 %

The reaction between copper and sulphuric acid is very regular in all cases, and sulphurous anhydride is evolved, no secondary reactions taking place.

Iron

Acetic Acid

Dilute acetic acid attacks iron readily with violent evolution of oxygen. Cailletot (Comptes Rendus, 68, 395) declares, however, that it is scarcely attacked by dilute or concentrated acetic acid when the latter is under high pressure.

Weak acetic acid, according to Storer (Dictionary of Chem-

ical Solubilities), acts very slowly, and the action, furthermore, is completely stopped by the addition of arsenious acid.

Alkalis

Concerning the action of alkalis on iron, there seems to be a decided divergence of opinion. Thus, according to Groschuff (Handbuch der Arbeitsmethoden in der anorganischen Chemie), iron becomes passive in solutions of the alkalis, while in Comey's Dictionary of Chemical Solubilities we find the statement that it is not attacked by them at all.

Venator (Dingl., 261, 133, and Chem. Zeitung, 10, 319) when evaporating soda lye found that iron was more violently attacked than copper, whereas Lunge (Chem. Ind., 1866, 47) found the corrosion of copper vessels greater than that of iron apparatus.

Again, according to Thomson (J. Soc. Ch. Ind., 15, 118) soda lye of various concentrations and temperatures does not attack iron; but when evaporating it, the rivets of the apparatus used were frequently torn up. Lunge (Dingl., 261, 131) declares that soda lye has slight action on iron between 15° and 100°.

Ammonia

Dilute ammonia has no effect on iron in presence of hydrogen peroxide.

Ammonia disintegrated iron completely between 400° and 900°.

Carulla (J. Steel Inst., 1908, I, 71) declares that cast-iron stills for ammonia prove everlasting. One such had been under his observation for 18 years, and was as sound and perfect as when erected. The reactions taking place in these stills were, of course, entirely basic, lime being used to expel the fixed portion of the alkali. Kempson & Co. (J. Iron Steel Inst., 1908, 83) confirm this from their experience.

Hydrochloric Acid

In the case of hydrochloric acid, the addition of small amounts of metallic salts influences the action. Weak acetic acid has

very little action, the addition of platinum chloride ($PtCl_4$) increases it, arsenious acid (As_2O_3) stops it; other solutions have no effect. With racemic and tartaric acids the phenomena are the same.

Iron is slowly soluble in hydrochloric acid, and the action is accelerated on heating. According to Molinari (Inorganic Chemistry), *chemically pure iron,* however, is insoluble in this acid.

If moist hydrochloric acid gas condenses on *cast iron,* the corrosion is very severe, but between 169°–371° C. this gas has little action, even if accompanied by water vapor. Above 426° it again attacks energetically.

Nitric Acid

In concentrated nitric acid *cast iron* becomes passive, and is then susceptible to the action of less concentrated acids; concentrated nitric acid can be despatched in iron containers.

When iron is treated with pure concentrated nitric acid of 1.512–1.419 sp. gr. it becomes covered with a bluish or black coating, and in this condition is not attacked by nitric acid of any strength at ordinary temperature or at the temperature of a freezing mixture; action occurs on heating, however. Nor is iron attacked at ordinary temperature by an acid of 1.401 sp. gr. or even somewhat weaker acid, though on heating action begins at once. Very dilute nitric acid attacks iron wire at the ordinary temperature. The action of nitric acid is influenced by platinum chloride ($PtCl_4$). The more water the acid contains the lower will be the temperature at which iron remains passive; shaking the wire hastens passivity. Contact with platinum, gold or carbon does not prevent it.

Passivity occurs with nitric acid of 1.38 sp. gr. after a short time at 31°; but if the temperature is 32°, passivity does not occur. Colorless nitric acid of 1.42 sp. gr. produces passivity at 55°, but not at 56°. Red fuming nitric acid of 1.42 sp. gr. produces passivity at 82°, but not at 83°.

Passivity depends on a coating of nitrous oxide (NO), which hinders the action of the acid. All operations which re-

move this layer terminate the passivity, such as shaking, rubbing, placing in a vacuum, etc.

The passivity ceases when iron is placed in dilute acid, after a longer or shorter time, according to the dilution of the acid.

When	acid	has	sp.	gr.	1.30,	after	11	days
"	"	"	"	"	1.28,	"	5	"
"	"	"	"	"	1.26,	"	32	hours
"	"	"	"	"	1.16,	"	12	"

(Varenne in Comptes Rendus, 68, 395.)

Iron is scarcely attacked by dilute or concentrated acids under high pressure. (Cailletet, Comptes Rendus, 68, 395.)

Iron is dissolved by nitric acid even when very concentrated, but no gas is evolved, and the process is very slow.

Nitric acid of the following sp. gr. dissolves the following amounts from strips of pure iron:

Sp. Gr. of Acid	Diminution of weight in 24 Hours
1.28	0.82%
1.34	0.75%
1.38	0.29%
1.48	0.34%
1.53	5.80%

Iron may be kept for almost any length of time in concentrated nitric acid without any action ensuing, while a dilute acid will act upon it with violence.

Iron dissolves in most dilute acids. Dilute nitric acid dissolves it in the cold. When placed in concentrated acid it appears to undergo a change, and is then not attacked by the acid ("passive state"); this condition may also be brought about, not only by the action of the nitric acid, but also of other substances, such as bromic, chloric, iodic and chromic acids, and even hydrogen peroxide, as well as by electrolysis, using the iron as anode in sulphuric acid.

* Comey, Dictionary.

Sulphuric Acid

Concentrated oil of vitriol acts very little indeed on cast iron, whether hot or cold, provided that air is excluded; dilute sulphuric acid, if the dilution be not too great, acts very little on cast iron in the cold or at a gentle heat if air is excluded.

At the ordinary temperature all sulphuric acids down to 106° Twaddell (50° Bé.) act very little on all descriptions of cast iron. At 100° the action is much stronger. It is least in the case of an acid of 168° Tw. (65.9 Bé.), 1½ times stronger with acid of 142° Tw. (60° Bé.), and three times stronger with an acid of 106° Tw. (50° Bé.).

At the boiling point the differences are far more pronounced. Acid of 168° Tw. acts very little even then, both in a pure state or as commercial acid (containing a little N_2O_3), or when containing a little SO_2. But acid of 142° Tw. acts fourteen times stronger at 200° than the same acid at 100° C., and twenty times stronger than acid of 168° Tw. At 285° commercial acid of 142° Tw. does not act very differently from pure acid of the same strength. Acid of 106° Tw. at its boiling point (= 147° C.) acts less than acid of 142° at 200° C., but still 14 times as much as acid of 168° Tw. at 295° C. There is no difference between pure and commercial acid in this case.

The differences between various mixtures of cast iron are of no importance against acid of 168° Tw. (5.9 Bé.) in all cases, and against the weaker acids at 20° and 100° C. But the latter acids at their boiling points act decidedly less on charcoal-pig and on chilled cast iron than on all other kinds. The differences between hot and cold casting have not been found.

The following mixtures were examined:

No. 1. White and grey charcoal-pig, melted in the cupola.
No. 2. The same, cast very cold.
No. 3. Ordinary machine casting, containing one-third scrap iron.
No. 4 Hard (chilled) coating (Special Mixture).

No. 5. 150 Clarence No. 3, 200 Hayenge No. 3, 200 scrap.
No. 6. 200 " " 75 " " 225 "
No. 7. 200 Harrington No. 4, 200 Coltness No. 1, 100 scrap.
No. 8. Coltness No. 1, pure.

The following table shows the loss of weight caused by one hour's action of sulphuric acid of various strengths and qualities at different temperatures:

Mixture No	a			b			c		
	Pure 20°	Acid 100°	168° Tw 295°	Pure 20°	Acid 100°	142° Tw 295°	Pure 20°	Acid 100°	106° Tw 295°
1 . .	0.016	0.096	0.075	0.018	0.156	1.539	0.015	0.265	1.107
2 .	0.028	0.099	0.103	0.016	0.160	1.581	0.026	0.277	1.083
3.	0.021	0.084	0.046	0.016	0.125	2.551	0.025	0.324	2.053
4.	0.017	0.082	0.096	0.010	0.154	1.551	0.027	0.236	1.323
5.	0.023	0.017	0.131	0.016	0.058	2.229	0.027	0.320	1.667
6	0.020	0.103	0.131	0.019	0.046	2.082	0.022	0.314	1.615
7	0.021	0.080	0.175	0.025	0.048	2.595	0.027	0.343	1.715
8. . .	0.025	0.100	0.133	0.017	0.019	2.639	0.037	0.323	1.952
Average...	0.021	0 095	0 113	0 018	0.149	2.096	0.026	0.300	1.564

Mixture No.	Commercial Acid				Acid of 168° Tw. cont. some Sod. Sulphite
	168° Tw		142° Tw	106° Tw	
	100° C	295° C	200° C	174° C	295° C
2	0.094	0.139	2.017	1.114	0.107
4.	0.069	0.124	2.007	1.368	0.107
5. .	0 102	0.156	2.248	1.671	0.106
6	0.074	0.152	2.645	1.981	0.136
Average	0 085	0 143	2 229	1 533	0.109

In concentrated sulphuric acid iron becomes passive, and is then susceptible to the action of less concentrated acids; this is especially true of cast iron. Concentrated sulphuric acid can be dispatched in iron flasks, or evaporated in iron bowls.

Iron is readily soluble in dilute sulphuric acid and most other acids. The action of sulphuric acid is very much accelerated by the addition of a few drops of platinum chloride ($PtCl_4$);

the addition of arsenious acid (As_2O_3) arrests the action completely. Tartar emetic and mercury chloride ($HgCl_2$) diminish the action, but do not arrest it. (Comey, Dictionary.)

Sulphuric acid has only a slow action on cast iron at the ordinary temperature with exclusion of air. Weak acids have a strong action at higher temperatures. Charcoal-pig iron and case-hardened cast iron are much less attacked by weak acids at the boiling point than other kinds of iron. Scotch pig iron is the most strongly attacked. (Comey, Dictionary.)

99.8 percent sulphuric acid has very slight action at the ordinary temperature when air is excluded. (Lunge, Dingl., 261, 131.)

Resistance against dilute sulphuric acid is greatly increased by increase in the amount of carbon (C) if chemically combined, less by silicon (Si). (Ledebur, Dingl., 223, 326.)

On the whole, cast iron withstands strong sulphuric acid very well, even when boiling. (Davis, Handbook.)

LEAD

Acetic Acid

Acetic acid attacks lead even in the cold, and dissolves it readily in presence of air.

Alkalis

Calcium hydroxide (CaO_2H_2) and caustic soda ($NaOH$) at tack lead much more actively in absence of carbon dioxide and presence of air. In absence of dissolved oxygen neither calcium hydroxide nor sodium hydroxide attacks lead.

Sodium carbonate (Na_2CO_3) in absence of carbon dioxide attacks lead slightly, but sodium bicarbonate ($NaHCO_3$) has not the slightest action. Calcium bicarbonate ($CaH_2(CO_3)_2$) also has no action, and the presence of calcium carbonate ($CaCO_3$) and carbon dioxide (CO_2) wholly prevents water attacking lead. The above reactions are not in the least altered by the presence of moderate amounts of ammonium or organic

compounds; but ammonium salts in excess have a strong solvent action upon lead.

Lead is somewhat soluble in sodium chloride (NaCl); the latter attacks this metal at high temperatures.

Alkali solutions oxidize lead when in contact with the air.

Ammonia

Ammonia rapidly corrodes lead.

Hydrochloric Acid

Lead is indifferent to hydrochloric acid if air is excluded. (Arndt, Technik, p. 491.) It is almost insoluble in cold, and only slowly attacked when boiling. (Comey, Dictionary.) Boiling concentrated hydrochloric acid has only very slight action on lead, according to Berzelius (quoted in Comey's Dictionary).

George E. Davis, on the other hand, declares in his "Handbook" that hydrochloric acid dissolves lead, while Molinari ("Inorganic Chemistry") states that this acid does not attack lead in the cold.

Nitric Acid

Lead is completely soluble in nitric acid if not too concentrated, but presence of sulphuric or hydrochloric acid diminishes the solvent power to a great extent. It is only slowly attacked by nitric acid of any strength below 15°; above 15° it is most strongly attacked by a rather weak acid.

That lead is not acted upon by very concentrated nitric acid is confirmed in Comey's "Dictionary." George E. Davis ("Handbook") declares that the action is very energetic if the acid is dilute, but more slow if concentrated. Molinari ("Inorganic Chemistry") states that nitric acid dissolves lead in the cold.

Sulphuric Acid

In "Berichte de Deutschen Chemischen Gesellschaft" (1775, 210), BAUER writes:

"50 grams of strongest oil of vitriol (168° Tw.—65.9 Bé.) with 0.2 gr. pure lead produce a sensible evolution of gas at 175°, stronger at 196°; at 230–240° all the lead is suddenly changed into sulphate, with formation of SO_2, H, and S.

"Lead containing varying quantities of bismuth is even more strongly acted upon, while small quantities of antimony and copper make it more resistant. Lead containing 10 percent tin behaves like pure lead."

LUNGE says in "Sulphuric Acid and Alkali," p. 658:

"Sulphuric acid of 144° Tw. (60.4 Bé.) or even up to 152° Tw. (62.3 Bé.) acts very little on lead, even when hot; and so long as the acid has not to be stronger than 144° Tw., lead on vessels can be used. It is not advisable, however, to use lead for concentrations above 144° Tw., because at that point the lead is much acted upon; and in no case can lead be used beyond 152° Tw., because in that case the boiling point of the acid too nearly approaches the temperature at which lead begins to soften, and also because the acid then acts too strongly upon it."

Going further into the subject, the same author continues, on p. 992:

"Since there are serious contradictions concerning the action of sulphuric acid on lead, I have undertaken, with Mr. E. Schmid, a thorough examination of the subject. Following are a few general results:

"Pure, soft lead suffers in all cases less chemical attack than hard lead, containing 1.8 percent antimony, or the alloy of 18 parts antimony and 82 parts lead. With the rise of temperature the differences increase very quickly.

"The presence of air in all cases increases the action.

"Sulphuric acid containing nitrous acid (nitrous vitriol) acts more strongly than pure acid at all temperatures and on all descriptions of lead."

According to DITTE (Annales Chim. Phys., 19, 68), lead is acted on by sulphuric acid only when concentrated and hot; the reaction is very regular in all cases, and sulphurous anhydride is evolved, no secondary reactions taking place.

HART states (J. Soc. Ch. Ind., 26, 504) that lead can be used for working with sulphuric acid if it is covered with a protective layer of lead sulphate, but that it is even then dissolved some times.

Lead is indifferent to sulphuric acid if air is excluded, according to ARNDT (" Technik," 491).

Sulphuric acid of 1.842 sp. gr. dissolves 201 gr. from 1 sq. meter pure lead at the ordinary temperature (time?) and sulphuric acid of 1.705 sp. gr. only 59 gr. Slight impurities lessen this solubility. (Calvert & Johnston, Chem. Soc. (2), 1, 66.)

Lead is strongly attacked by 99.8 percent sulphuric acid at the ordinary temperature with exclusion of air (Lunge, Dingl., 261, 131). Also strongly attacked by pure cold concentrated sulphuric acid (99.78 percent H_2SO_4); lead vessels that contained the acid were gradually destroyed. (Napier and Tatlock, Chem. News, 42, 314.)

The action of sulphuric acid on lead is slight, even at high temperatures, until sp. gr. 1.75 has been exceeded, when action becomes energetic, boiling acid of 1.84 acting very severely, and fuming still more so. (George E. Davis, Handbook.)

Sulphuric acid does not attack lead in the cold (Molinari, " Inorganic Chemistry ").

Lead is scarcely attacked by sulphuric acid. (Kodosdy, Chemische Laboratoriums-Praxis.)

TIN

Acetic Acid

Tin resists acetic acid very well in the cold.

Alkalis

Tin is soluble in alkali lye and in aqueous solutions of the alkalis. It resists alkalis very well in the cold.

Hot caustic soda (NaOH) dissolves it, and potassium lye (potassium hydroxide) does so on warming.

When digested with alkali lye, tin gradually dissolves.

Ammonia

Tin is not soluble in ammonia.

Hydrochloric Acid

Tin is slowly soluble in dilute cold hydrochloric acid, but rapidly if hot and concentrated.

Nitric Acid

Tin is violently attacked by concentrated nitric acid with precipitation of stannous (tin) oxide (SnO_2). It is completely soluble in dilute cold nitric acid (1 part HNO_3, 1 part water) at 22°.

It is not attacked by pure concentrated nitric acid of 1.512–1.419 sp. gr., but violently by less concentrated acid; it is likewise attacked by most concentrated acid if it contains nitrous oxide (NO_2).

If tin is placed in dilute nitric acid of 1.15 sp. gr. it is slowly dissolved, but soon precipitated again as SnO_2. If a small amount of ammonium chloride (NH_4Cl) is added, the tin remains permanent in solution. Hydrochloric acid has a similar action.

Nitric acid and water containing less than 12 percent HNO_3 attacks tin and forms a stannous salt, which decomposes, giving a turbid solution. Nitric acid and water (12–45 percent HNO_3) completely dissolves tin, but the solution becomes turbid on standing. If it contains more than 45 percent HNO_3 it does not dissolve tin, but forms a white substance, which is soluble in water if over 70 percent acid is used; this solution soon becomes turbid.

Tin is transformed into the insoluble oxide by nitric acid. By somewhat diluted nitric acid it is converted into metastannic acid.

Sulphuric Acid

Tin is slowly soluble in hot dilute sulphuric acid, but decomposed by hot concentrated. (Hay, Chem. News, 22, 208.)

Tin is not dissolved by dilute sulphuric acid. (Arndt, "Technik," page 491.)

Tin is easily soluble in the cold in a mixture of 1 vol. H_2SO_4, 2 vols. HNO_3, and 3 vols. H_2O.

Dilute sulphuric acid does not attack tin in the cold, and only slowly on warming. (Heppe, "Die Chemischen Reaktionen.")

ZINC

Acetic Acid

Dilute acetic acid dissolves zinc very easily, but not when zinc is very pure.

Alkalis

Zinc is very slowly soluble in caustic potash, but quickly in contact with iron (Arndt, "Technik," p. 495).

Zinc is easily soluble in alkalis, even ammonium hydrate (NH_4OH), especially when the zinc is in contact with iron; in sodium chloride (NaCl) with precipitation of ZnO; in saturated alkali chlorides. (Comey, "Dictionary.")

Zinc dissolves in solutions of the alkalis with evolution of hydrogen, the zinc peroxide first formed dissolving in the excess of alkali. It is also slowly soluble in warm aqueous solutions of caustic potash.

Ammonia

Zinc is slowly soluble in ammonia.

Hydrochloric Acid

Zinc is very slowly soluble in dilute hydrochloric acid in glass vessels if the zinc is pure. When fused at the lowest temperature, it is much more slowly soluble than when heated to a red heat. (Comey, "Dictionary.")

Hydrochloric acid, pure or dilute, attacks zinc in the cold, and dissolves it without warming being necessary (Arndt, "Technik," p. 495.)

Nitric Acid

Zinc is not attacked by nitric acid of 1.512–1.419 sp. gr. at a temperature of — 18° or less, but violently if the temperature is raised. Acid of 1.419–1.401 sp. gr. does not attack zinc at the temperature of a freezing mixture, but violently at 0°. More

dilute acid attacks zinc even at — 20°. (Comey, "Dictionary.")

Zinc dissolves in nitric acid (Roscoe and Schorlemmer, "Treatise on Chemistry," II).

Dilute nitric acid dissolves zinc. (Heppe, "Die Chemischen Reaktionen.")

Sulphuric Acid

Dilute sulphuric acid dissolves given percent zinc in the same length of time (B = according to Bolley, R = according to Rammelsberg).

	Slowly Cooled		Rapidly Cooled	
	B	R	B	R
Cast at melting point	42.5	74.1	13.0	9.9
Cast at a red heat.	100.0	69.4	85.5	9.5

Sulphuric acid, pure and dilute, attacks zinc even in the cold, and dissolves it without warming being necessary (Arndt, "Technik," p. 495).

50 cc. sulphuric acid dissolved in two hours the following amounts from 1 sq. cm. of zinc at $t°$:

t°C	Strength of Acid	Gms Dissolved
20	H_2SO_4	0.000
130	H_2SO_4	0.075
150	H_2SO_4	0.232
20	$H_2SO_4H_2O$	0.002
130	$H_2SO_4H_2O$	0.142
150	$H_2SO_4H_2O$	0.345
20	$H_2SO_42H_2O$	0.002
130	$H_2SO_42H_2O$	4.916
150	$H_2SO_42H_2O$	3.450
20	$H_2SO_43H_2O$	0.005
130	$H_2SO_43H_2O$	3.080
20	$H_2SO_44H_2O$	0.049
130	$H_2SO_44H_2O$	0.456
20	$H_2SO_45H_2O$	0.027
130	$H_2SO_45H_2O$	0.337
20	$H_2SO_46H_2O$	0.018
100	$H_2SO_46H_2O$	3.16

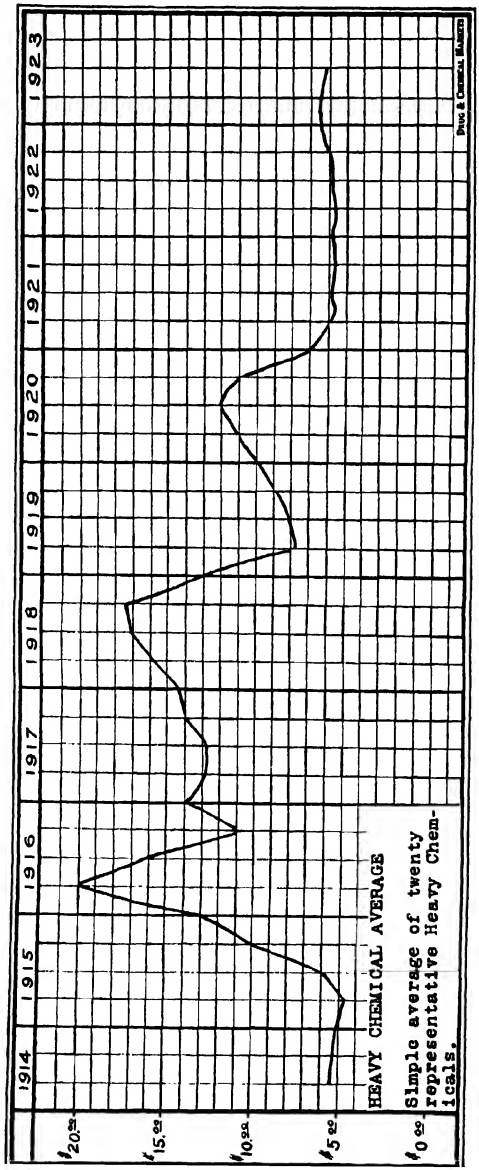
C. P. zinc is more quickly soluble in dilute acids in vacuo than under normal pressure, the ratio being about 1 : 6.5. The rate of solubility increases slowly with rise of temperature from 0° to 98°, when it amounts to about four times that at 0°, but from 98° to 100° the increase is thirteenfold. Thus, as an average of six experiments, dilute sulphuric acid (1 : 20) dissolves in thirty minutes 2.1 mg. zinc at 0°; 4.0 mg. at 20°; 7.4 mg. at 60°; 9.3 mg. at 98°, but 122.1 mg. at 100°. If, however, the acid is prevented from boiling by increasing the pressure, the sudden increase between 98° and 100° does not take place.

The rate of solubility in dilute sulphuric acid (1 : 20) is also increased 175 times by the addition of chromium trioxide (CrO_3), and 306 times by the addition of hydrogen dioxide (H_2O_2).

The solubility of zinc in acids is very much affected by the presence of small quantities of various metallic salts. Small amounts of platinum chloride ($PtCl_4$) accelerate the action 149 times, and arsenous oxide (As_2O_3) 123 times. Mercuric chloride ($HgCl_2$) has a strong retarding action, owing to the precipitation of mercury on the zinc.

Pure zinc is very slowly dissolved by dilute sulphuric acid; when heated with concentrated, sulphur dioxide (SO_2) is evolved, but no hydrogen sulphide is produced. (Roscoe and Schorlemmer, " Treatise on Chemistry," vol. 2.)

Cold concentrated sulphuric acid attacks zinc but slightly but the metal is dissolved on heating. Dilute sulphuric acid dissolves zinc readily. (Heppe, " Die Chemischen Reaktionen. ")



Courtesy Drug and Chemical Markets.

Prices of Intermediates

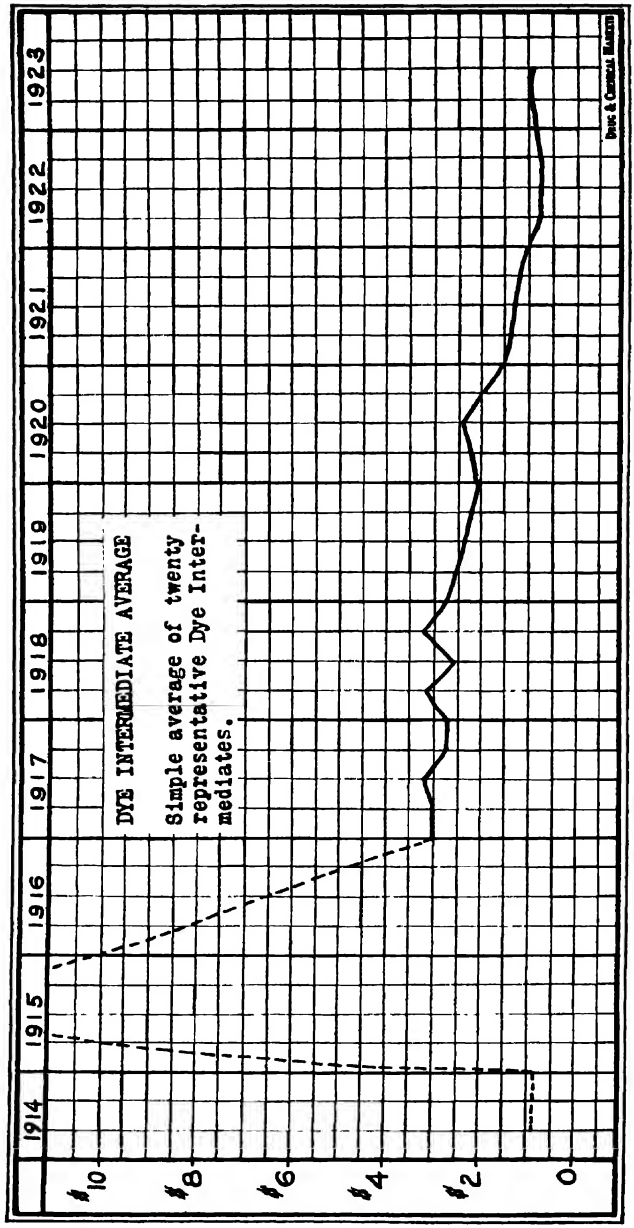
		1914		1915				1916				1917				1918			
		Sept	Dec.	Mar	June	Sept	Dec.	Mar.	June	Sept	Dec	Mar	June	Sept	Dec	Mar.	June	Sept.	Dec.
Benzene, Pure	c 1 gal	.26	.34	1.10	.75	.90	.80	.90	.80	.60	.55	.55	.58	.51	.40	.31	.25½	.25	.20
Naphthalene, Flake	*lb.	.02⅜	.03	.04¾	.15	.16	.13	.15	.10½	.08	.09½	09½	.09¼	.08¾	.09¾	.10½	.09¼	.08½	.07¼
Phenol	*lb.	.08½	.45	.50	1 20	1.50	1.40	1.35	1.10	.65	.57½	.55	.46	.42	.43	.56	.53	.46½	.43	.30
Phthalic Anhydride	lb	—	—	—	—	—	—	—	—	—	—	—	6.40	6.40	6.40	4.60	3.80	4.25	3.25
Aniline Oil	lb	.10½	nom.	1.00	1.15	1 40	95	85	.50	.28	22	.28	.30	26½	.26½	25¾	.27¼	.28½	.28
Benzidine Base	lb.	—	—	—	—	—	—	—	—	2 25	1.90	1.75	1.85	1.85	1.80	1.75	1.75	1.75	1.70
Dimethylaniline	lb.	—	—	—	—	—	1 25	1.10	.75	.70	.57	.55	.58	.60	.60	.63¾	.69	.76	.75
Dinitrobenzene	lb.	—	—	—	—	—	—	—	—	.45	.40	.45	.33	.33	.33	.34	.34	.35	.40
Diphenylamine	lb	—	—	—	—	—	—	—	1.50	1.00	.90	.85	.90	.90	1.00	.90	.90	1.05	1.00
Beta-naphthol	lb	.08	—	—	—	—	1.50	1.50	1.35	1 15	1.15	.70	.75	.63	.65	.65	.60	.65	.60
Alpha-naphthylamine	lb	—	—	—	—	—	—	—	1.25	1.25	1.25	1.25	1.15	.80	.70	.62	.60	.61	.55
Para-nitroaniline	lb	08	—	—	—	—	—	—	1.60	1.50	1.30	1.25	1.25	1.25	1.10	1.05	1.70	1.85	1.40
Para-phenylenediamine	lb.	—	—	—	—	—	—	5.00	5.00	4.50	3.50	3.50	3.50	3.50	3.50	3.50	3.50	4.00	3.25
Para-toluidine	lb.	—	—	—	—	—	—	—	—	—	—	—	.95	.95	.95	.95	.95	.85	.85
R-Salt	lb	—	—	—	—	—	—	—	—	1.90	1.70	1.75	1.90	2.00	2.25	2.25	2.05	2.05	2.00

Courtesy Drug and Chemical Markets.

Prices of Intermediates—(Continued)

		1919				1920				1921				1922				1923	
		Mar	June	Sept.	Dec	Mar.	June	Sept.	Dec	Mar.	June	Sept.	Dec.	Mar.	June	Sept.	Dec.	Mar.	June
Benzene, Pure	per gal.	.22	.24	.25	.25	.27	.27	.35	.30	.30	.30	.27	.27	.29	.29	.30	.30	.30	.27
Naphthalene, Flake	*lb.	.02⅜	.08½	.06	06	.07	.08½	.16	.16½	.09	.08½	.08	.06½	.06½	.07½	.07	.07	.06	.06½	.08½
Phenol	*lb.	.08½	.08	.11½	.12	.19	.27	.23	.17	.11	.10	.09	.08	.10	.12½	.12	.20	.35	.50	.50
Phthalic Anhydride	lb.		2.25	1.80	.80	.60	.75	45	.50	.65	.55	.55	.40	.40	.35	.35	.35	.35	.35	.32
Aniline Oil	lb.		.24	.22	.30	.33	.34	.35	.27½	.22	.22	.19	.18	.17	.16	.14	.14	.16	.16	.16
Benzidine Base	lb.		1.35	.90	1.00	1 25	1.40	1.35	1.25	1.00	85	1 00	1.00	.90	.90	.85	.85	.85	.82	.82
Dimethylaniline	lb.		.57	.50	.55	90	1.30	1.25	.80	.75	.55	.42	.45	.45	.38	.36	.30	.39	.42	.42
Dinitrobenzene	lb		.34	.32	.23	.26	.43	.35	.32	.29	.33	.25	.25	.21	.21	.20	.20	.19	.19	.19½
Diphenylamine	lb		.75	.70	.53	65	.80	.85	.80	.70	.60	.60	.65	.65	.60	.58	.54	.52	.48	.48
Beta-naphthol	lb.		.55	.40	.45	.55	.55	.85	.80	.42	.34	.38	.32	.30	.28	.23	.22	.23	.23	.23
Alpha-naphthylamine	lb.		.45	.35	.32	.33	.40	.60	.50	.40	.38	.38	.35	.27	.30	.30	.30	.28	.30	.35
Para-nitroaniline	lb.		1.35	.95	.95	1.15	1.35	1.65	1.10	1.05	.85	.80	.79	.77	.77	.75	.75	.73	.74	.74
Para-phenylenediamine	lb.		3.25	2.75	2.75	2.25	2.50	2.65	2.55	2.20	1.75	1.75	1.70	1.60	1.50	1.50	1.50	1.50	1.50	1.45
Para-toluidine	lb.		.85	.85	.62½	.62½	.75	.90	.90	.85	.85	.70	.60	.60	1.00	1.00	.95	1.00	.90	.90
R-Salt	lb.		1.75	1.50	1 50	1.75	1.75	2.00	1.70	1.75	1.25	1.25	1.25	1.25	.60	.54	.50	.55	.55	.55

*August 1914 price.


DYE INTERMEDIATE AVERAGE
Simple average of twenty representative Dye Intermediates.
1914
1915
1916
1917
1918
1919
1920
1921
1922
1923
$10
$8
$6
$4
$2
0

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